

**Insensitive high-performance replacements for RDX in
explosive and propellant formulations**

Interim Technical Report

by

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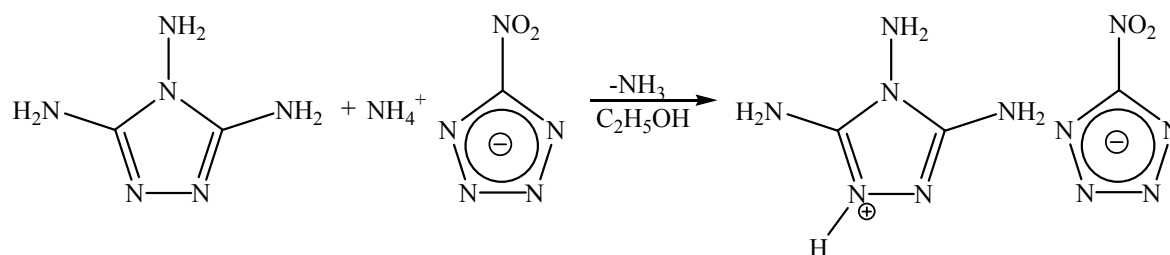
Research Plan

The objective of the proposed research project is to investigate and explore the chemistry of neutral (covalent) high-nitrogen compounds and high-nitrogen salts as potential energetic ingredients for gun propellant charges and replacements for RDX. The new high-nitrogen compounds and salts should be less environmentally hazardous, have no greater sensitivities, and have equal or better performance.

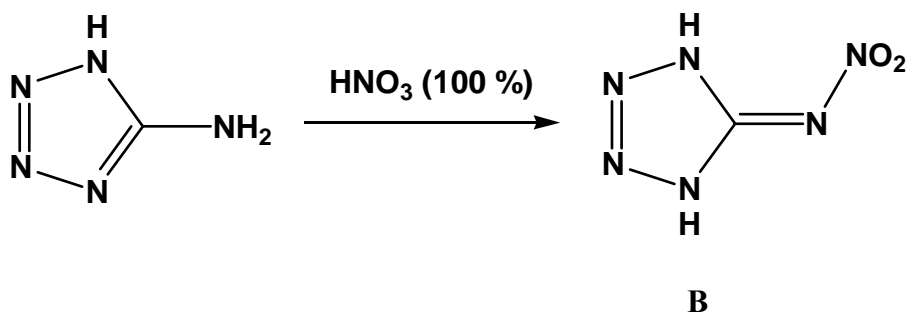
Research Schedule

Year 2007 (original proposal and additional work as specified in January 07):

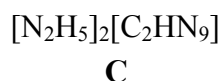
- (i) Delivery of 5-gram quantities of the following energetic materials to ARL:
 - 5-Aminotetrazolium nitrate
 - 1-Methyl-5-aminotetrazolium nitrate
 - 1,4-Dimethyl-5-aminotetrazolium nitrate
 - 1,4-Dimethyl-5-aminotetrazolium perchlorate
 - 1,4-Dimethyl-5-aminotetrazolium azide
 - 1,4-Dimethyl-5-aminotetrazolium dinitramide
 - Guanidinium-5-nitrotetrazolate
 - Aminoguanidinium-5-nitrotetrazolate
 - 1,4-Dimethyl-5-aminotetrazolium-5,5'-azotetrazolate dihydrate
- (ii) Synthesis and experimental determination of the heat of combustion and sensitivity data of 1-Methyl-5-methylnitramino tetrazole:
(O₂N)(CH₃)N-C-N(CH₃)NNN
- (iii) Synthesis and full analytical and spectroscopic characterization of energetic high-nitrogen salts of 3,4,5-triamino-triazole (see Structure A).



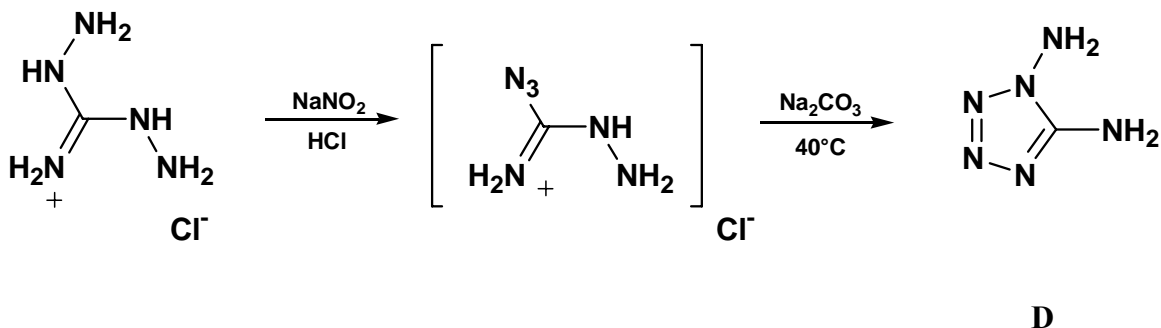
- (iv) Synthesis and full analytical and spectroscopic characterization of neutral energetic high-nitrogen compounds of nitrated 5-aminotetrazoles (see Structure **B**).



- (v) Synthesis and full analytical and spectroscopic characterization of energetic high-nitrogen salts of dihydrazinium bistetrazolato amine (see Structure **C**).



- (vi) Synthesis and full analytical and spectroscopic characterization of energetic high-nitrogen salts of diaminotetrazole (see Structure **D**).



- (vii) Structural (X-ray) characterization of selected energetic high-nitrogen salts and neutral compounds of structural types **A**, **B**, **C** and **D**.
- (viii) Experimental evaluation of the sensitivities of all energetic high-nitrogen neutral compounds and salts of structural types **A**, **B**, **C** and **D**.: friction sensitivity, impact sensitivity, thermal sensitivity.
- (ix) Scale-up of the energetic high-nitrogen salts of aminotetrazole from laboratory scale (2 g quantities) to larger quantities (50 – 100 g) in order to carry out initial performance tests (Koenen test, steel sleeve test)

Part I: Amino and nitrated aminotetrazoles

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Experimental

1. 1-(N-Methyl-N-nitramino-methyl)-5-aminotetrazol

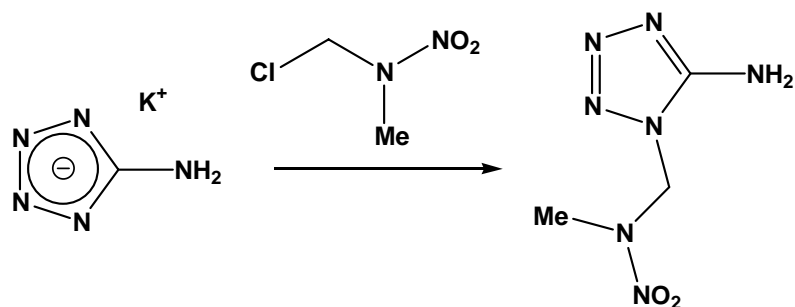


Fig. Reaction equation

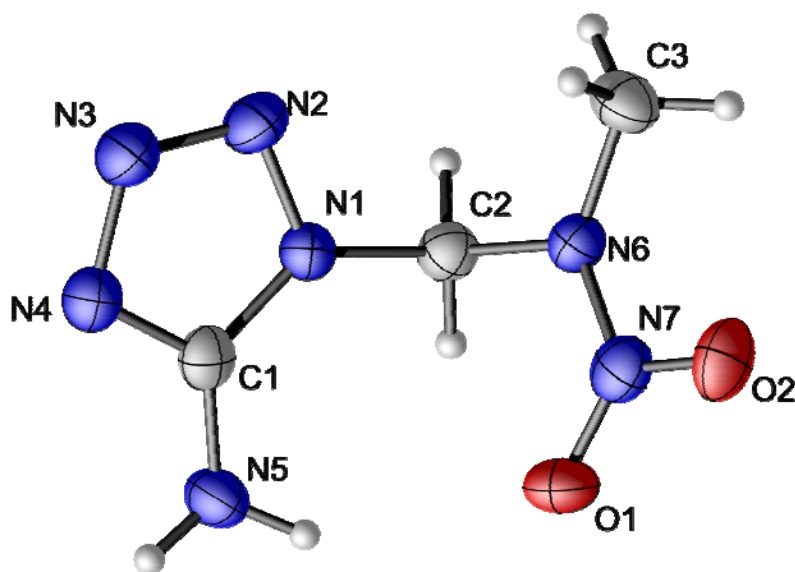


Fig. Molecular unit with labelling scheme

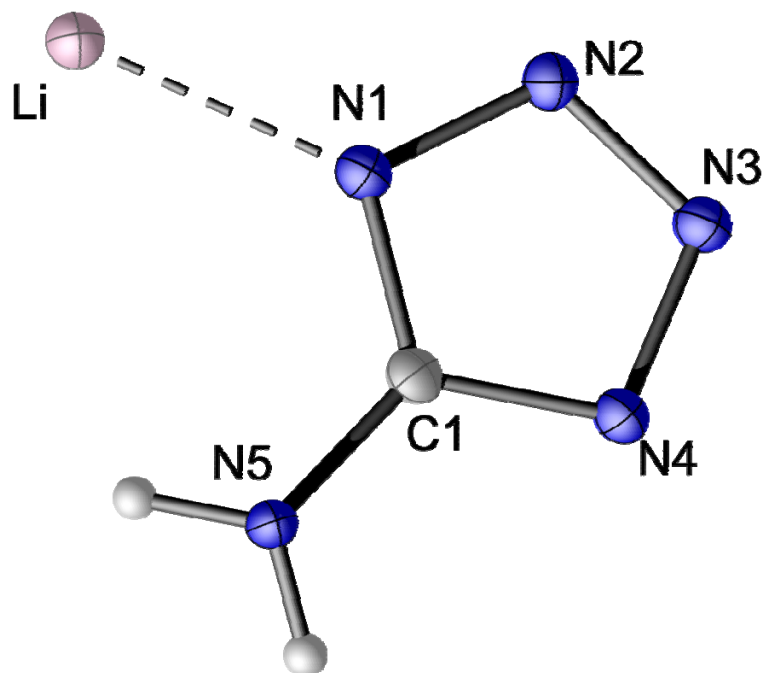
m.p.: 140 °C (DSC, 5°/min) ; IR (KBr, cm⁻¹) $\tilde{\nu}$ = 3424 (s), 3238 (m), 3137 (w), 3036 (w), 2924 (w), 1623 (s), 1580 (m), 1522 (m), 1471 (w), 1420 (w), 1384 (m), 1297 (m), 1261 (s), 1202 (w), 1117 (w), 1074 (w), 1020 (w), 991 (w), 794 (w), 655 (w), 604 (w), 441 (w); Raman (1064 nm, 200 mW, 25 °C, cm⁻¹): $\tilde{\nu}$ = 3038 (36), 2995 (35), 2962 (28), 1648 (11), 1582 (13), 1528 (9), 1468 (12), 1440 (19), 1424 (17), 1355 (19), 1314 (19), 1262 (41), 1126 (15), 1094 (13), 1019 (12), 925 (13), 849 (100), 794 (56), 714 (8), 655 (15), 604 (23), 472 (29), 445 (30), 397 (24), 303 (20), 233 (23), 196 (21); ¹H NMR ([d6]-DMSO, 25°C, ppm) δ : 6.94 (s, 2H, -NH₂), 6.10 (s, 2H, -CH₂-), 3.43 (s, 3H, -CH₃); ¹³C NMR ([d6]-DMSO, 25°C) δ : 156.2 (CN₄), 59.5 (-CH₂-), 39.3 (-CH₃); ¹⁴N NMR ([d6]-DMSO, 25°C) δ : -30.4 (NO₂); ¹⁵N NMR([d6]-DMSO,25°C) δ : 7.1 (N3), -26.7 (N2), -29.9 (NO₂), -94.5 (N4), -176.3 (N1), -205.2 (N-NO₂), -33.7 (NH₂, t, ¹J (N-H) = 88.6 Hz); *m/z* (DEI⁺): 173 [M]⁺ (2), 99 (8), 89 (98), 73 (3), 59 (5), 57 (2), 46 (4), 44 (12), 43 (100), 42 (67), 42 (6), 40 (2), 30 (11), 28 (34), 27 (6); EA (C₃H₇N₇O₂, 173.13): calcd.: C 20.81, H 4.08, N 56.63, O 18.48; BAM-Drophammer: < 30 J; BAM-Friction Test: < 360 N; $\Delta U_{\text{comb.}}$: 3342 cal/g, ΔH_f : 234 kJ/mol

Energetic properties (Calculations using EXPLO5):

| 2 | |
|---|---|
| Formula | C ₃ H ₇ N ₇ O ₂ |
| Molecular Mass | 173.13 |
| Impact sensitivity (J) ^a | > 30 J |
| Friction sensitivity (N) ^b | > 360 N |
| Electrical discharge | no reaction |
| N (%) | 56.63 |
| Ω (%) ^d | -69.31 |
| Combustion | yes |
| T _{dec.} (°C) | 122 |
| Density (g/cm ³) | 1.62766 |
| -ΔU _{comb.} (cal/g) | 3342 |
| -ΔH _{comb.} [°] (kJ/mol) | 2416 |
| Δ _f H _m [°] (kJ/mol) | 234 |
| -Δ _E U _m [°] (J/g) | 4520 |
| T _E (K) | 3136 |
| p (kbar) | 244 |
| D (m/s) | 8106 |

2. Alkali Aminotetrazolates

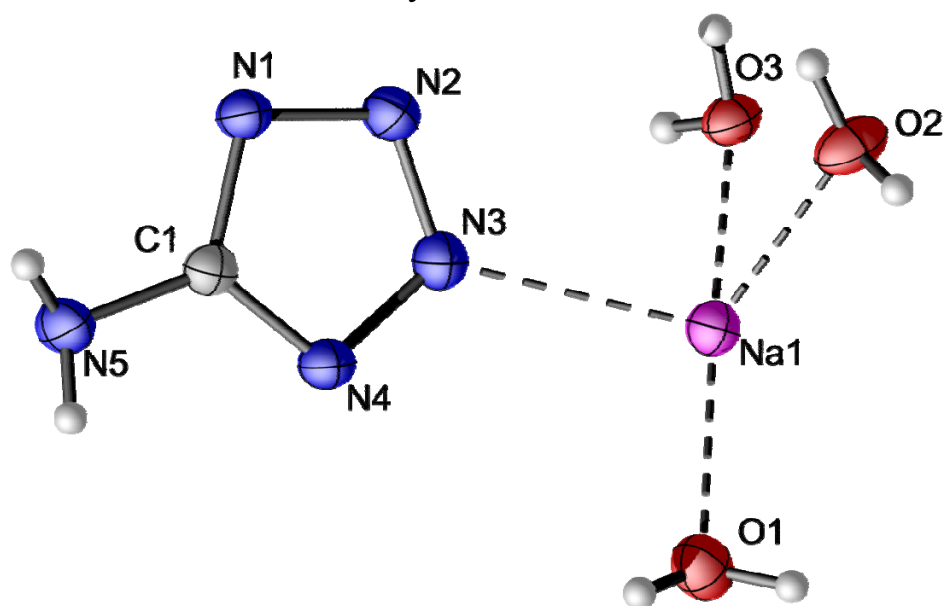
2.1 Lithium 5-aminotetrazolate



5-Aminotetrazole (8.51 g, 0.1 mole) and lithium hydroxide (2.40 g, 0.1 mole) were combined and solved in 50 ml of hot water. The water was evaporated and the crude product was recrystallized from hot ethanol obtaining colorless prisms suitable for XRD. (8.65 g, yield 95 %)

m.p.: 197°C ; IR (KBr, cm^{-1}) $\tilde{\nu}$ = 3484 (s), 3383 (s), 3275 (s), 3198 (s), 2933 (m), 2776 (m), 2631 (m), 2507 (m), 1775 (m), 1670 (s), 1641 (s), 1451 (m), 1298 (m), 1243 (s), 1159 (m), 1062 (s), 995 (s), 915 (m), 756 (m), 741 (m), 690 (w), 547 (s); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3259 (29), 3205 (33), 2614 (18), 1694 (33), 1634 (24), 1450 (45), 1298 (77), 1155 (43), 1095 (82), 1053 (64), 996 (49), 759 (100), 437 (59), 139 (52); EA (CH_2LiN_5 , 91.00): calcd.: C 13.20; H 2.22; Li 7.63; N 76.96 %; found: C 13.03; H 2.30; N 75.79 %.

2.2 Sodium 5-aminotetrazolate trihydrate

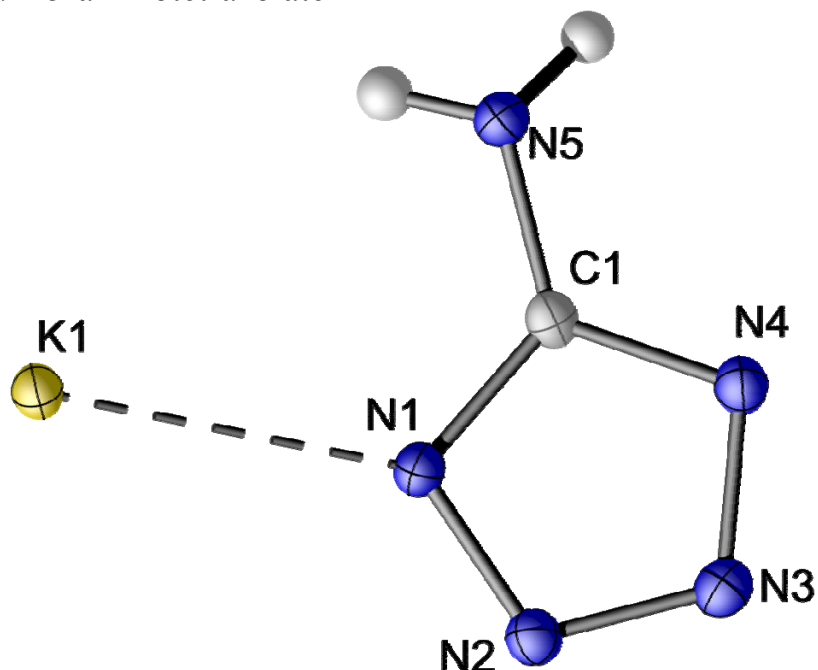


5-Aminotetrazole (8.51 g, 0.1 mole) and sodium hydroxide (4.0 g, 0.1 mole) were added to 50 ml water and refluxed for 2 minutes. The water was evaporated and the colorless product was recrystallized from a small amount of water. The colorless needles could be determined using X-ray diffraction. (14.98 g, yield 93 %)

m.p. 306 °C; IR (KBr, cm^{-1}) $\tilde{\nu}$ = 3591 (s), 3415 (s), 3389 (s), 3266 (s), 3190 (s), 2267 (w), 1644 (s), 1520 (s), 1454 (m), 1298 (w), 1233 (m), 1137 (m), 1111 (m), 1067 (m), 1011 (w), 848 (m), 800 (m), 756 (m), 717 (m), 594 (m); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3178 (39), 1512 (59), 1450 (49), 1235 (94), 1114 (45), 1069 (100), 853 (35), 745 (55), 403 (39), 152 (41); EA ($\text{CH}_8\text{N}_5\text{NaO}_3$, 161.10): calcd.: C 7.46; H 5.01; N 43.47; Na 14.27; O 29.79 %; found: C 7.61; H 4.72; N 44.28 %.

:

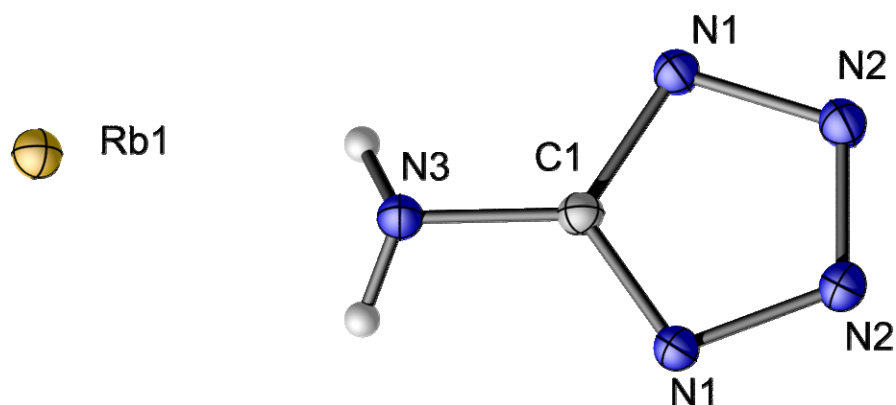
2.3 Potassium 5-aminotetrazolate



5-Aminotetrazole (8.51 g, 0.1 mole) and potassium hydroxide (5.61 g, 0.1 mole) were added to 50 ml water and refluxed for 2 minutes. The water was evaporated and the colorless product was recrystallized from a small amount of water. The colorless rods were suitable for X-ray diffraction. (11.20 g, yield 91 %)

m.p. 267 °C; IR (KBr, cm^{-1}) $\tilde{\nu}$ = 3390(s), 3310 (m), 3325 (m), 2730 (w), 2241 (w), 2137 (w), 1737 (w), 1704 (w), 1688 (w), 1637 (s), 1635 (s), 1564 (m), 1502 (vs), 1473 (m), 1454 (s), 1208 (s), 1139 (s), 1111 (s), 1057 (m), 1008 (m), 802 (s), 744 (m), 687 (m), 665 (m), 484 (w); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3390 (9), 3313 (16), 3229 (6), 1631 (3), 1517 (53), 1445 (11), 1207 (57), 1142 (4), 1114 (20), 1058 (100), 1010 (4), 799 (4), 742 (27), 426 (14), 151 (6), 132 (11); EA (CH_2KN_5 , 123.16): calcd.: C 9.75, H 1.64, K 31.75, N 56.86 %; found: C 9.73; H 1.68; N 56.48 %.

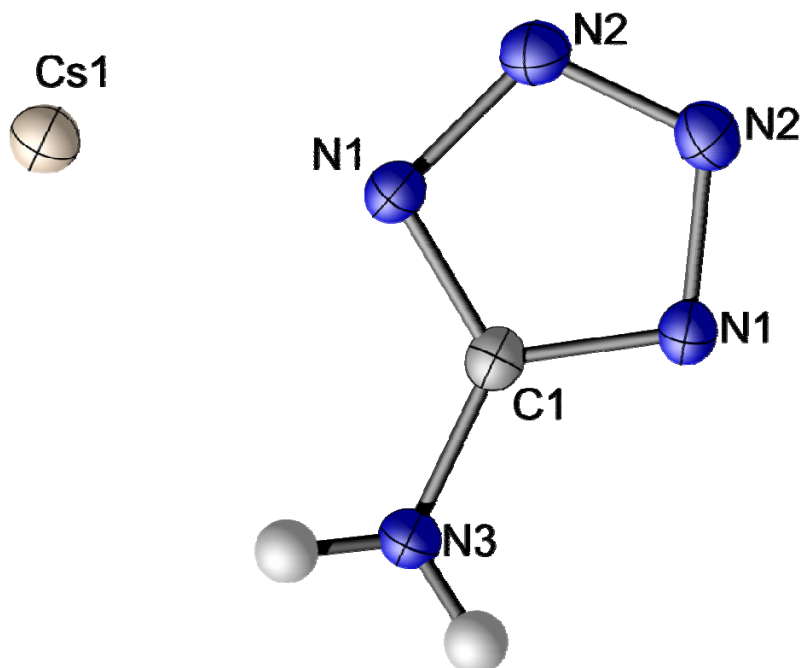
2.4 Rubidium 5-aminotetrazolate



5-Aminotetrazole (8.51 g, 0.1 mole) and rubidium carbonate (11.55 g, 0.05 mole) were added to 50 ml water and refluxed for 5 minutes till the release of CO₂ stopped. The water was evaporated and the colorless product was recrystallized from hot ethanol. The colorless plates were suitable for X-ray diffraction.

m.p. 238 °C; IR (KBr, cm⁻¹) $\tilde{\nu}$ = 3391 (s), 3310 (s), 3226 (s), 2240 (w), 1633 (s), 1515 (s), 1454 (m), 1208 (m), 1138 (m), 1111 (m), 1058 (w), 1008 (w), 805 (m), 745 (m), 707 (m), 689 (m); Raman (1064 nm, 200 mW, 25 °C, cm⁻¹): $\tilde{\nu}$ = 3283 (85), 1509 (62), 1453 (9), 1223 (90), 1109 (34), 1054 (100), 750 (40), 411 (37), 340 (8), 159 (40); EA (CH₂N₅Rb, 168.94): calcd.: C 7.08; H 1.19; N 41.31, Rb 50.42 %; found: C 7.14; H 1.18; N 41.50 %.

2.5 Caesium 5-aminotetrazolate

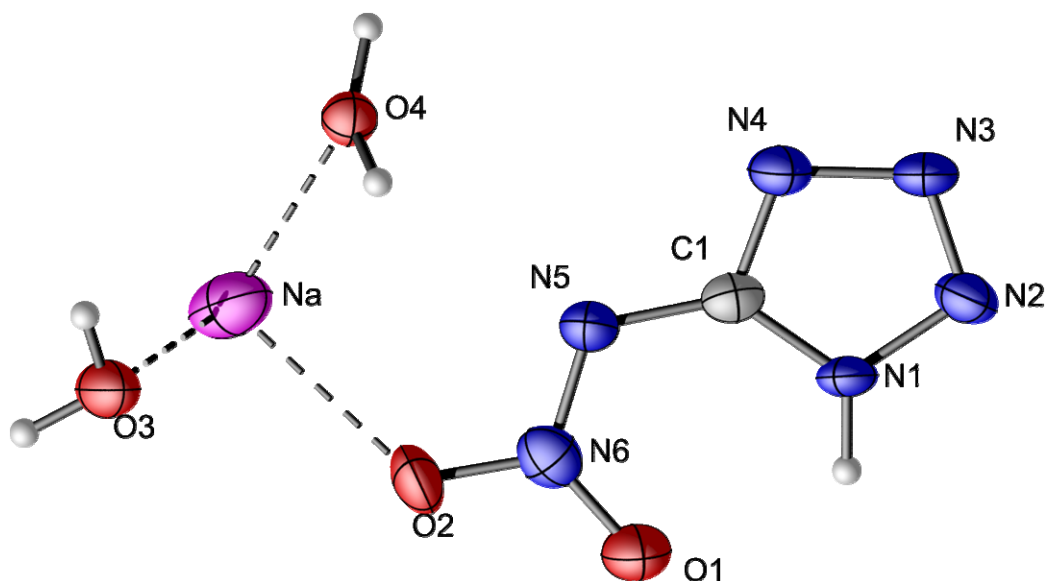


5-Aminotetrazole (8.51 g, 0.1 mole) and caesium carbonate (16.29 g, 0.05 mole) were added to 50 ml water and refluxed for 5 minutes till the release of CO₂ stopped. The water was evaporated and the colorless product was recrystallized from hot ethanol. The colorless plates were suitable for X-ray diffraction. (20.60 g, yield 95 %)

m.p. 267 °C; IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3372 (s), 3214 (s), 2762 (m), 2257 (m), 2133 (m), 1643 (S), 1523 (s), 1508 (s), 1453 (s), 1384 (m), 1239 (w), 1221 (m), 1137 (s), 1111 (s), 1050 (m), 1004 (8m), 782 (s), 746 (m), 721 (m), 669 (m), 477 (m); Raman (1064 nm, 200 mW, 25 °C, cm⁻¹): $\tilde{\nu}$ = 3358 (7), 3296 (13), 3201 (7), 1506 (56), 1450 (17), 1209 (70), 1108 (29), 1050 (100), 1005 (9), 749 (35), 408 (24), 342 (11), 136 (15); EA (CH₂CsN₅, 216.97): calcd.: C 5.54, H 0.93, Cs 61.26, N 32.28 %; found: C 5.56; H 0.95; N 32.29 %.

3. Metal salts of Nitriminotetrazol

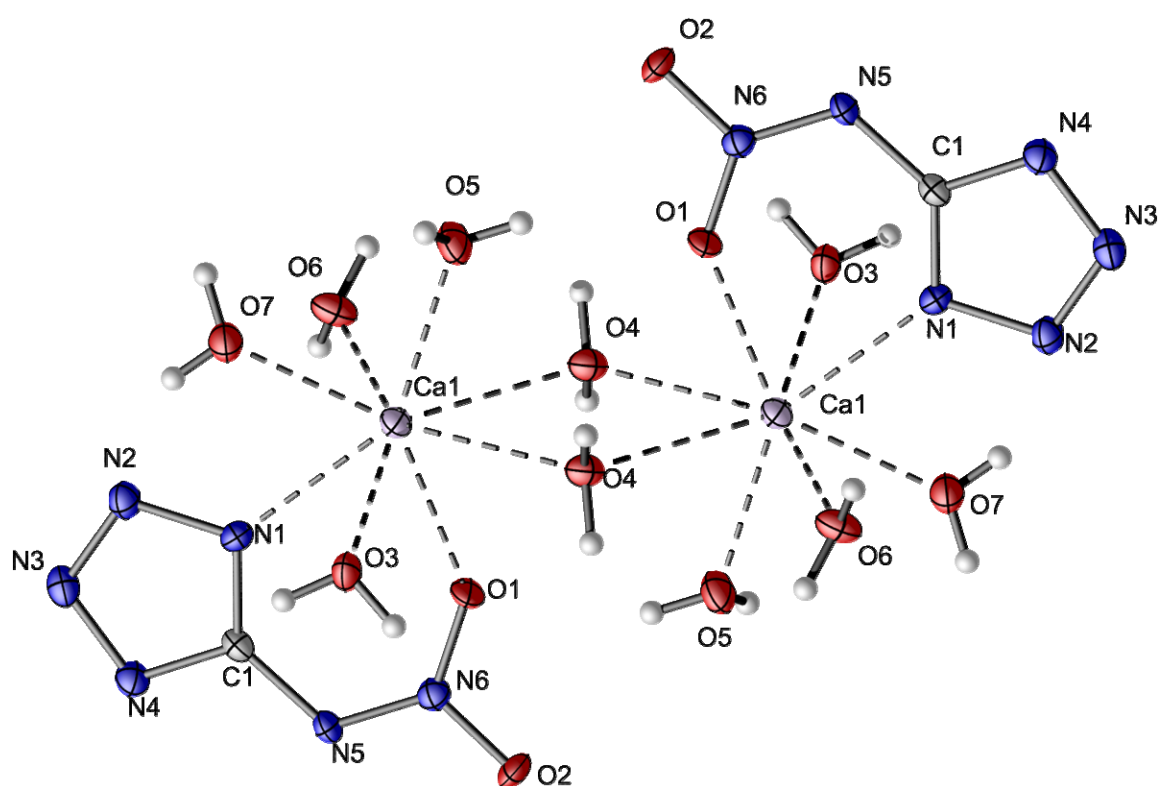
3.1 Sodium nitriminotetrazolate



Sodium hydroxide (0.16 g, 4 mmole) was solved in water and added to solved 5-nitriminotetrazole (0.58 g, 4 mmole). The water was evaporated and the colorless product was recrystallized from hot ethanol. The colorless needles were suitable for X-ray diffraction. (0.48 g, yield 79 %)

dec.: 214°C; IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3511 (m), 3364 (m), 3281 (m), 2960 (m), 2759 (m), 2349 (w), 1786 (w), 1673 (m), 1540 (m), 1436 (m), 1323 (s), 1240 (m), 1152 (m), 1063 (m), 999 (m), 869 (m), 771 (m), 742 (s), 698 (m), 555 (m); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 2981 (2), 1548 (100), 1446 (9), 1396 (9), 1368 (11), 1330 (37), 1151 (6), 1072 (7), 1019 (62), 871 (5), 752 (12), 485 (11), 413 (10), 375 (11), 243 (10); EA ($\text{C}_2\text{H}_8\text{N}_{12}\text{Na}_2\text{O}_7$, 358.14): calcd.: C 6.71, H 2.25, N 46.93, Na 12.84, O 31.27 %; found: C 6.79, H 2.36, N 46.74%.

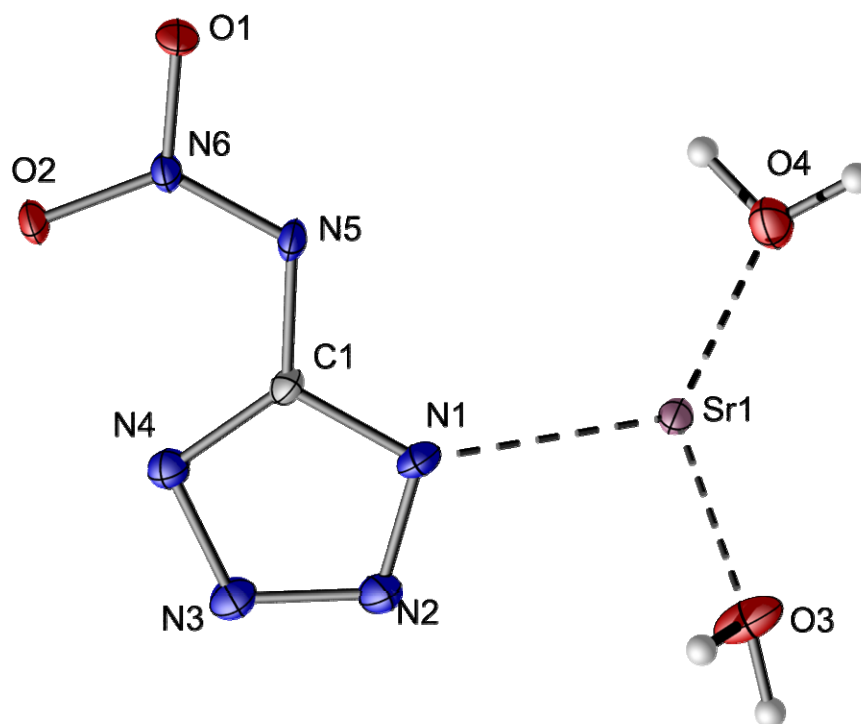
3.2 Calcium nitriminotetrazolate



5-Nitriminotetrazole (2.6 g, 20 mmole) was solved in 20 ml water, added to 120 ml solution of calcium hydroxide (1.48 g, 20 mmole) and refluxed for 3 min. Yellow crystals precipitated over night. The yellowish rods were suitable for X-ray diffraction. (0.48 g, yield 79 %)

dec.: 388°C; IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3745 (w), 3532 (m), 3359 (s), 3308 (s), 2448 (w), 2166 (w), 1976 (w), 1646 (m), 1622 (m), 1540 (w), 1474 (s), 1412 (s), 1338 (m), 1298 (s), 1157 (m), 1135 (m), 1087 (m), 1026 (s), 883 (m), 834 (m), 754 (m), 721 (w), 610 (w); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 2981 (2), 1487 (96), 1431 (9), 1406 (6), 1220 (7), 1160 (8), 1138 (7), 1091 (9), 1047 (7), 1029 (18), 727 (5), 611 (5), 406 (9); EA ($\text{CH}_{10}\text{CaN}_6\text{O}_7$, 258.20): calcd.: C 4.65, H 3.90, N 32.55, Ca 15.52; O 43.37 %; found: C 4.66, H 3.65, N 32.54%.

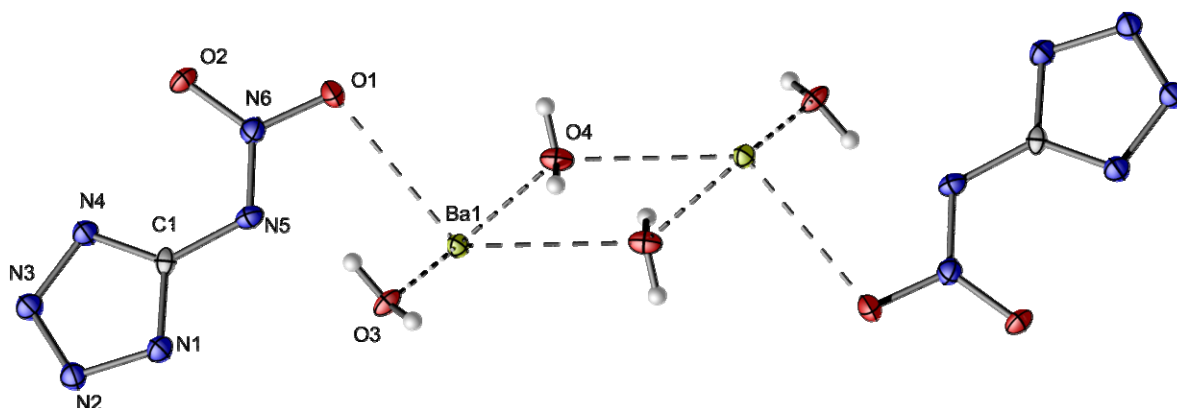
3.3 Strontium nitriminotetrazolate



5-Nitriminotetrazole (3.9 g, 0.03 mole) and strontium hydroxide octahydrate (7.97 g, 0.03 mole) were added to 40 ml water and refluxed for 3 minutes. After filtration, the crude product was recrystallized from hot ethanol obtaining colorless rods suitable for XRD. (6.7 g, yield 89 %)

m.p. : 235 °C, dec.: 348 °C; IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3454 (s), 3335 (s), 2484 (w), 2435 (w), 2342 (w), 1957 (w), 1548 (m), 1465 (s), 1418 (s), 1396 (s), 1313 (m), 1257 (m), 1160 (m), 1138 (w), 1082 (m), 1016 (m), 869 (m), 829 (w), 753 (m), 726 (w), 593 (m); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 1956 (0), 1462 (100), 1314 (1), 1214 (3), 1164 (4), 1142 (4), 1085 (3), 1035 (4), 1025 (22), 881 (1), 752 (1), 494 (1), 422 (8), 406 (2), 262 (2), 164 (2), 136 (1); EA ($\text{CH}_4\text{N}_6\text{O}_7\text{Sr}$, 251.70): calcd.: C 4.77, H 1.60, N 33.39, O 25.42, Sr 34.81 %; found: C 4.73, H 1.96, N 32.35 %.

3.4 Barium nitriminotetrazolate

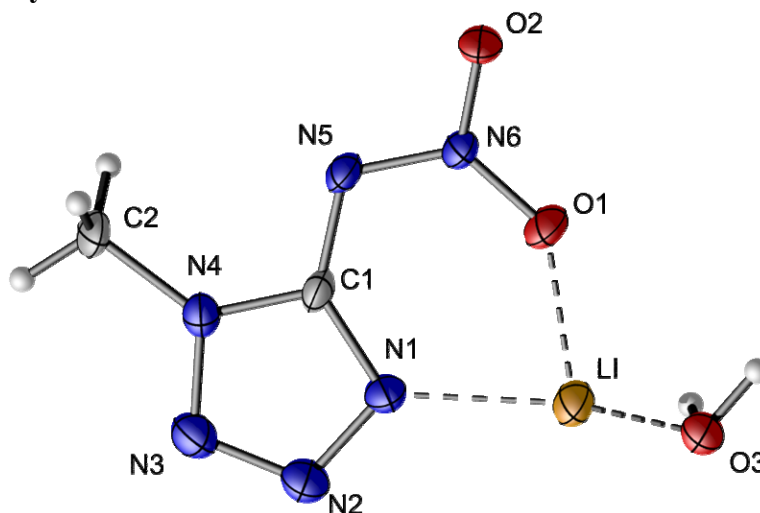


5-Nitriminotetrazole (3.5 g, 0.027 mole) was solved in 20 ml water and added to 25 ml of a barium hydroxide octahydrate (8.5 g, 0.027 mole) solution. Additionally 50 ml water was added and the solution refluxed for 10 minutes. After filtration, the crude product was recrystallized from hot ethanol obtaining light orange needles suitable for XRD. (2.38 g, yield 29 %)

dec.: 366°C; IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3443 (m), 3210 (m), 2341 (w), 2173 (w), 1651 (m), 1462 (s), 1405 (s), 1385 (s), 1304 (s), 1138 (m), 1079 (m), 1038 (m), 1018 (m), 880 (m), 835 (w), 772 (w), 751 (w), 695 (m), 564 (m); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3215 (4), 2537 (2), 1450 (85), 183 (7), 1215 (10), 1142 (7), 1082 (3), 1039 (4), 1015 (24), 881 (1), 767 (1), 705 (1), 492 (2), 428 (5), 400 (6), 259 (1), 152 (3); EA ($\text{CH}_4\text{BaN}_6\text{O}_4$, 301.41): calcd.: C 3.98, H 1.34, Ba 45.56, N 27.88, O 21.23 %; found: C 4.15, H 1.39, N 27.96 %.

4. Metal Salts of 1-Methylnitriminotetrazole

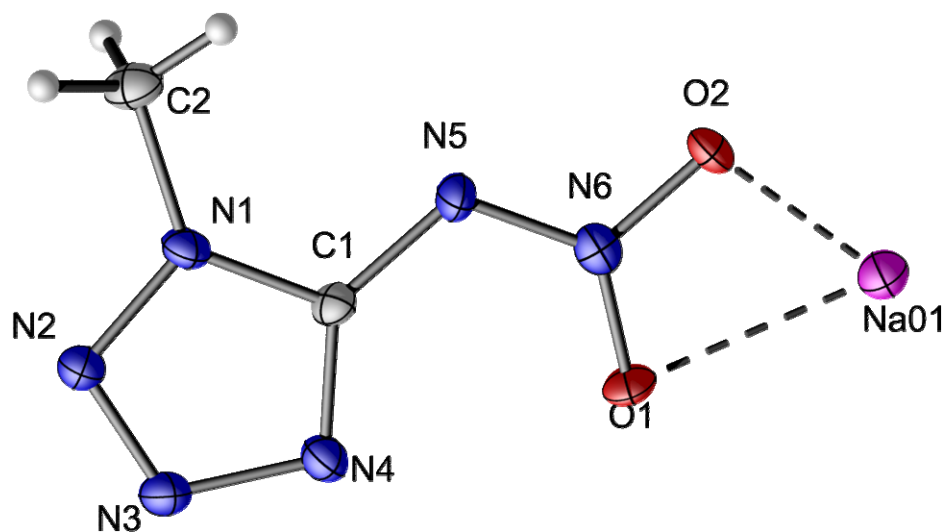
4.1 Lithium 1-methyl-5-nitriminotetrazolate



1-Methyl-5-nitriminotetrazole (0.64 g, 0.0044mmole) and lithium hydroxide (0.106 g, 0.0044 mmole) were both solved in 20 ml water. Afterwards the solution were combined and the water evaporated. The colorless rods could be determined using X-ray diffraction. (0.41 g, yield 61 %)

m.p.: ; IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3375 (m), 3319 (m), 3041 (w), 2973 (w), 2231 (w), 1668 (w), 1520 (m), 1481 (m), 1422 (m), 1319 (s), 1295 (s), 1242 (m), 1118 (m), 1055 (m), 999 (m), 893 (m), 769 (m), 739 (m), 683 (s), 584 (s); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3314 (2), 3037 (84), 2973 (15), 1522 (100), 1481 (15), 1450 (11), 1427 (21), 1401 (13), 1321 (23), 1297 (20), 1120 (18), 1047 (96), 1000 (5), 896 (12), 777 (13), 689 (22), 498 (15), 362 (8), 298 (28); EA ($\text{C}_2\text{H}_5\text{LiN}_6\text{O}_3$, 168.04): calcd.: C 14.29, H 3.00, Li 4.13, N 50.01, O 28.56 %;

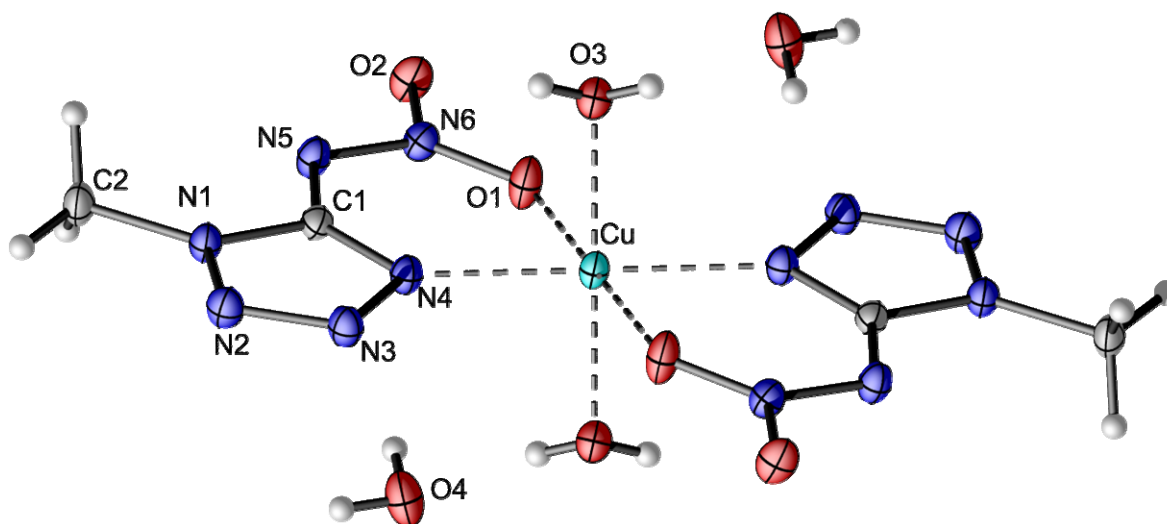
4.2 Sodium 1-methyl-5-nitriminotetrazolate



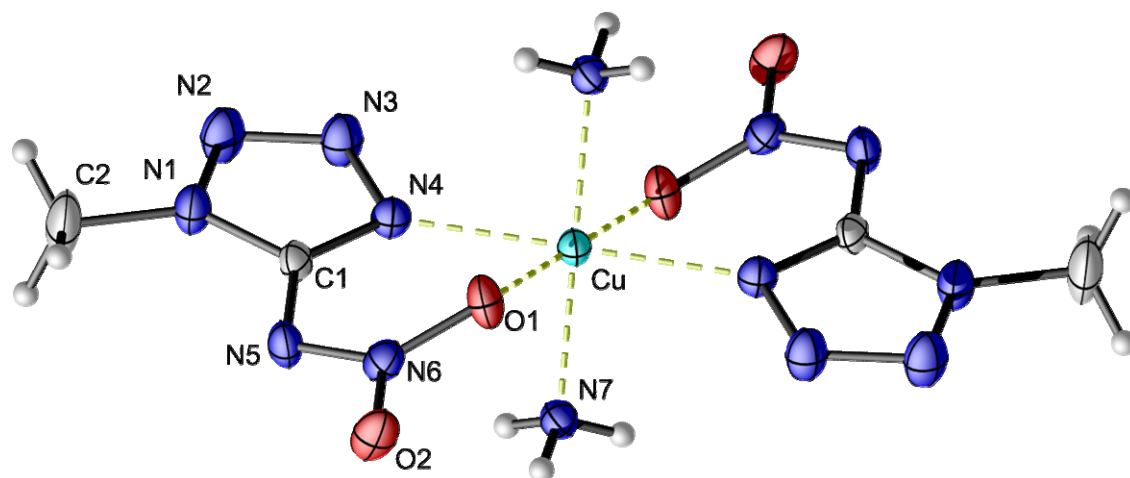
m.p.: ; IR (KBr) $\tilde{\nu}$ [cm^{-1}]: ; Raman (1064 nm, 200 mW) $\tilde{\nu}$ [cm^{-1}]: ; EA (CH_2CsN_5 , 216.97): calc.: C 5.54 %, H 0.93 %, Cs 61.26 %, N 32.28 %; found:

5. Copper Nitriminotetrazolates

5.1 Bis(1-methylnitriminotetrazolate)copper(II) tetrahydrate



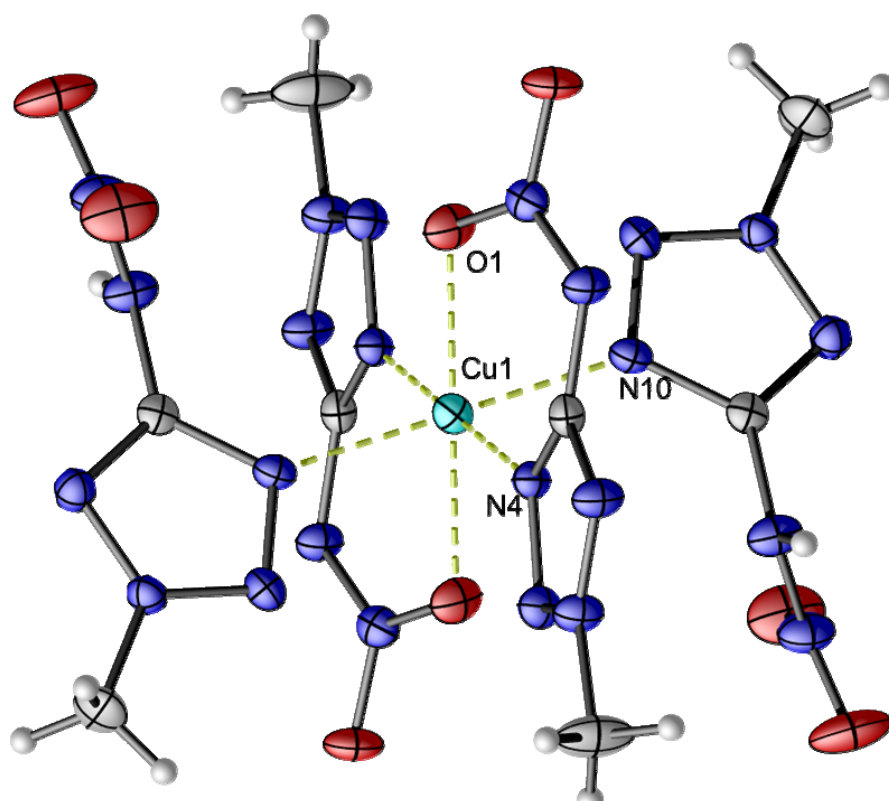
3.2 Diamino-bis(1-methylnitriminotetrazolate)copper(II)



Copper nitrate (483.2 mg, 2 mmole) was solved in 2 ml of hot ammonia (25 %). After solving 5-nitramino-1-methyl-tetrazole (576 mg, 4 mmole) in 10 ml of hot ammonia (25%), both solution were combined and refluxed for 5 min. The obtained purple cubic crystals were suitable for X-ray diffraction. (0.75 g, 98 %)

m.p.: 257 °C (dec.) (DSC, 5°/min) ; IR (KBr) $\tilde{\nu}$ [cm^{-1}]: 3504 (s), 3461 (m), 3220 (m), 1963 (m), 2416 (w), 2148 (w), 1622 (w), 1526 (s), 1476 (s), 1420 (m), 1398 (m), 1384 (s), 1339 (m), 1305 (vs), 1256 (s), 1120 (w), 1068 (w), 1037 (m), 1010 (w), 929 (w), 887 (w), 859 (w), 776 (w), 762 (w), 737 (w), 695 (w), 654 (w), 585 (w), 509 (w); Raman (1064 nm, 200 mW) $\tilde{\nu}$ [cm^{-1}]: ;EA (CH_2CsN_5 , 216.97): calc.: C 5.54 %, H 0.93 %, Cs 61.26 %, N 32.28 %; found:

3.3 Bis(2-methylnitriminotetrazolate)bis(2-methylnitraminotetrazole)copper(II)





Part II: Report about work on Pyrotechnics till March 07

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Aim: The goal of this work is finding new compounds, substituting barium in green pyrotechnic compositions, potassium as well as other perchlorates in red colorant pyrotechnics and new white burning mixtures based on high nitrogen compounds.

Index

1. Red colorants

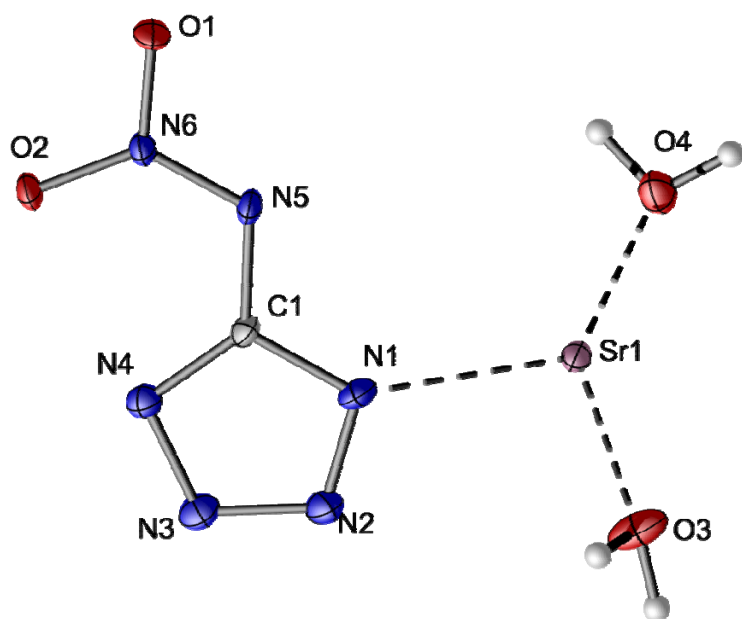
- 1.1 strontium nitriminotetrazolate dihydrate
- 1.2 strontium bis-(1-methyl-5-nitraminotetrazolate) monohydrate
- 1.3 lithium 1-methyl-5-nitraminotetrazolate monohydrate

2. Green colorants

- 2.1 *trans*-Tetra-aqua-bis-5-nitriminotetrazolato-*N*(4) copper(II)
- 2.2 triamino-5-nitraminotetrazolato- *N,O* copper (II)
- 2.3 *trans*-Bis[amino-(1-methylnitriminotetrazolate)] copper(II) dihydrate
- 2.4 *trans*-Diamino-bis(1-methylnitriminotetrazolate) copper(II)

Experimental

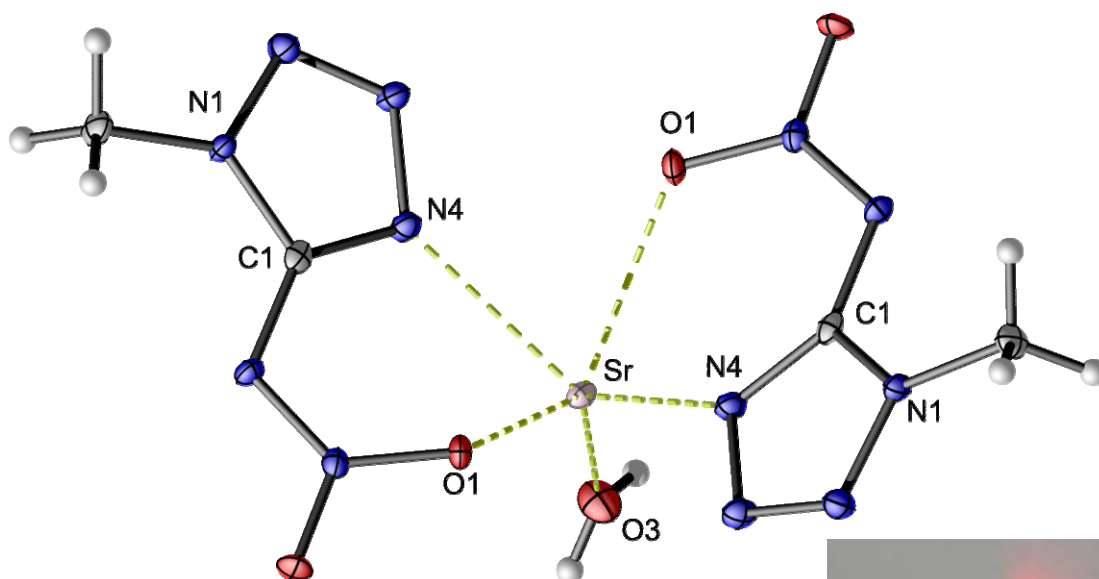
1.1 Strontium nitriminotetrazolate dihydrate



5-Nitriminotetrazole (3.9 g, 0.03 mole) and strontium hydroxide octahydrate (7.97 g, 0.03 mole) were added to 40 ml water and refluxed for 3 minutes. After filtration, the crude product was recrystallized from hot ethanol obtaining colorless rods suitable for XRD. (6.7 g, yield 89 %)

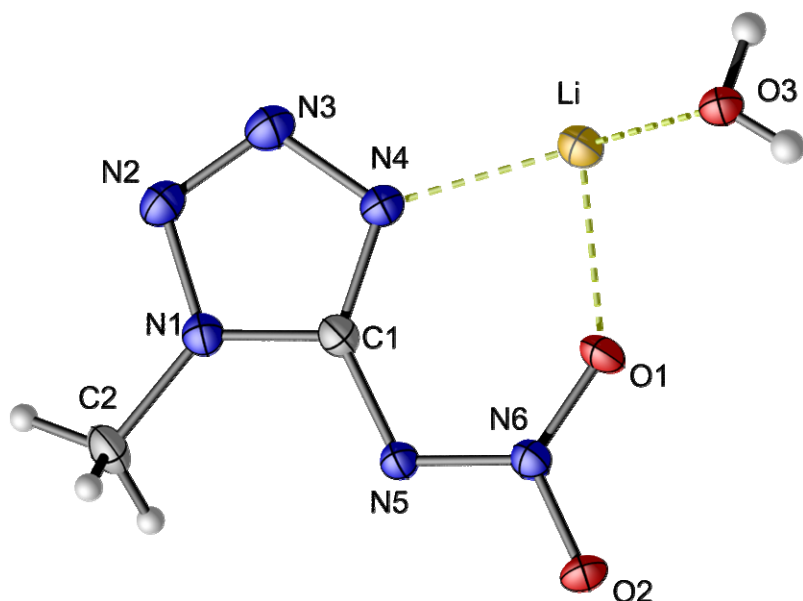
m.p.: 235 °C, dec.: 348 °C; **IR** (KBr, cm^{-1}): $\tilde{\nu}$ = 3454 (s), 3335 (s), 2484 (w), 2435 (w), 2342 (w), 1957 (w), 1548 (m), 1465 (s), 1418 (s), 1396 (s), 1313 (m), 1257 (m), 1160 (m), 1138 (w), 1082 (m), 1016 (m), 869 (m), 829 (w), 753 (m), 726 (w), 593 (m); **Raman** (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 1956 (0), 1462 (100), 1314 (1), 1214 (3), 1164 (4), 1142 (4), 1085 (3), 1035 (4), 1025 (22), 881 (1), 752 (1), 494 (1), 422 (8), 406 (2), 262 (2), 164 (2), 136 (1); **EA** ($\text{CH}_4\text{N}_6\text{O}_7\text{Sr}$, 251.70): calcd.: C 4.77, H 1.60, N 33.39, O 25.42, Sr 34.81 %; found: C 4.73, H 1.96, N 32.35 %.

1.2 Strontium bis-(1-methyl-5-nitraminotetrazolate) monohydrate



m.p.: 120 °C (-H₂O), 352 °C (dec.); **IR** (KBr, cm⁻¹): $\tilde{\nu}$ = 3552 (m), 3047 (w), 2963 (w), 2399 (w), 1617 (m), 1517 (s), 1470 (s), 1422 (s), 1388 (vs), 1375 (vs), 1335 (vs), 1294 (s), 1242 (s), 1115 (m), 1056 (m), 1025 (s), 990 (m), 879 (m), 771 (m), 761 (m), 738 (m), 704 (w), 693 (m), 502 (w), 466 (w); **Raman** (1064 nm, 200 mW, 25 °C, cm⁻¹): $\tilde{\nu}$ = 2966 (12), 1514 (100), 1470 (35), 1419 (9), 1376 (16), 1346 (30), 1299 (24), 1236 (3); **¹H NMR** (D₂O, 25°C) δ : 3.85 (H₂O), 4.78 (3H, CH₃); **¹³C NMR** (D₂O, 25°C) δ : 33.0 (CH₃), 156.0 (CN₄); **¹⁴N NMR** (D₂O, 25°C) δ : -18.5 (NO₂); **EA** (C₄H₈N₁₂O₅Sr, 391.8): calcd.: C 12.26, H 2.06, N 42.90, Sr 22.36 %; found: C 12.26, H 2.17, N 4.16 %.

1.3 Lithium 1-methyl-5-nitraminetetrazolate monohydrate

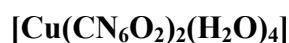
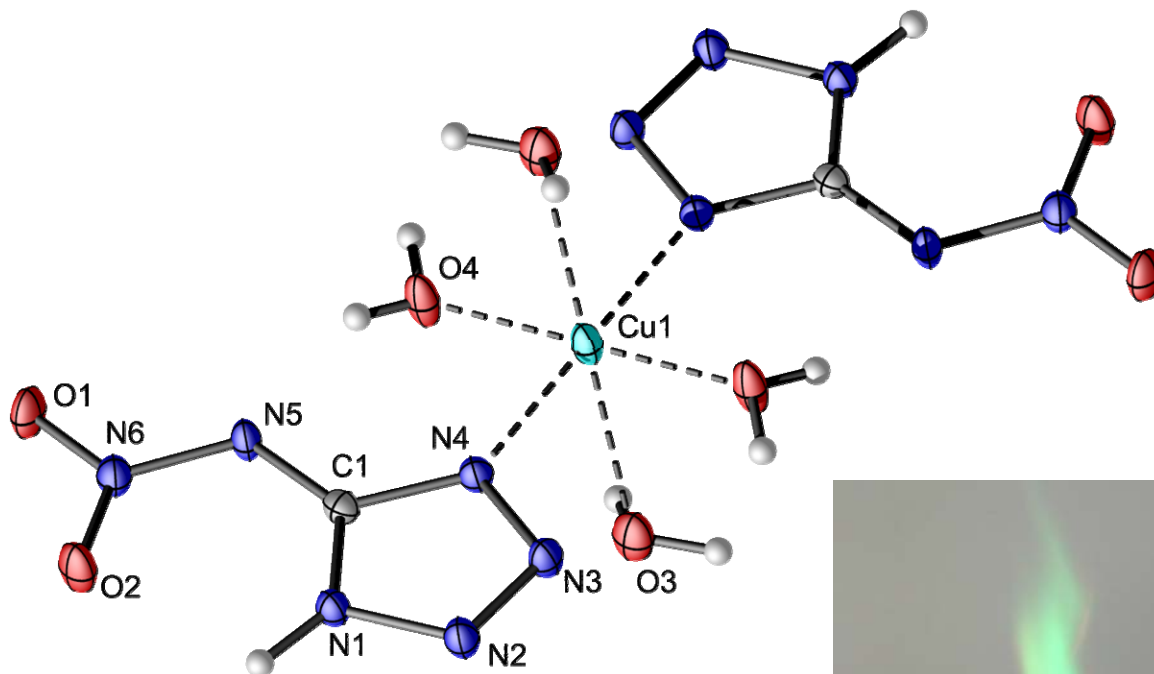


1-Methyl-5-nitraminetetrazole (0.64 g, 4.4 mmol) and lithium hydroxide (0.106 g, 4.4 mmol) were solved in 20 mL of warm water. Afterwards the two solutions were combined and the water was evaporated. The colorless rods could be determined using X-ray diffraction. (0.41 g, yield 61 %)

m.p.: 271 °C, 301 °C (dec.); **IR** (KBr, cm^{-1}): $\tilde{\nu}$ = 3375 (m), 3319 (m), 3041 (w), 2973 (w), 2231 (w), 1668 (w), 1520 (m), 1481 (m), 1422 (m), 1319 (s), 1295 (s), 1242 (m), 1118 (m), 1055 (m), 999 (m), 893 (m), 769 (m), 739 (m), 683 (s), 584 (s); **Raman** (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3314 (2), 3037 (4), 2973 (15), 1522 (100), 1481 (15), 1450 (11), 1427 (21), 1401 (13), 1321 (23), 1297 (20), 1120 (18), 1047 (96), 1000 (5), 896 (12), 777 (13), 689 (22), 498 (15), 362 (8), 298 (28); **^1H NMR** ([d6]-DMSO, 25 °C, ppm) δ : 3.45 (s, crystal water), 3.62 (s, -CH₃), 3.80 (d); **^{13}C NMR** ([d6]-DMSO, 25°C, ppm) δ : 33 (s, CH₃) 164.4; **EA** (C₂H₅LiN₆O₃, 168.04): calcd.: C 14.29, H 3.00, Li 4.13, N, 50.01, O 28.56 %; found: C 14.27, H 3.10, N, 49.95 %, ΔU_c : -2000 cal/g.

2. Copper Nitriminotetrazolates

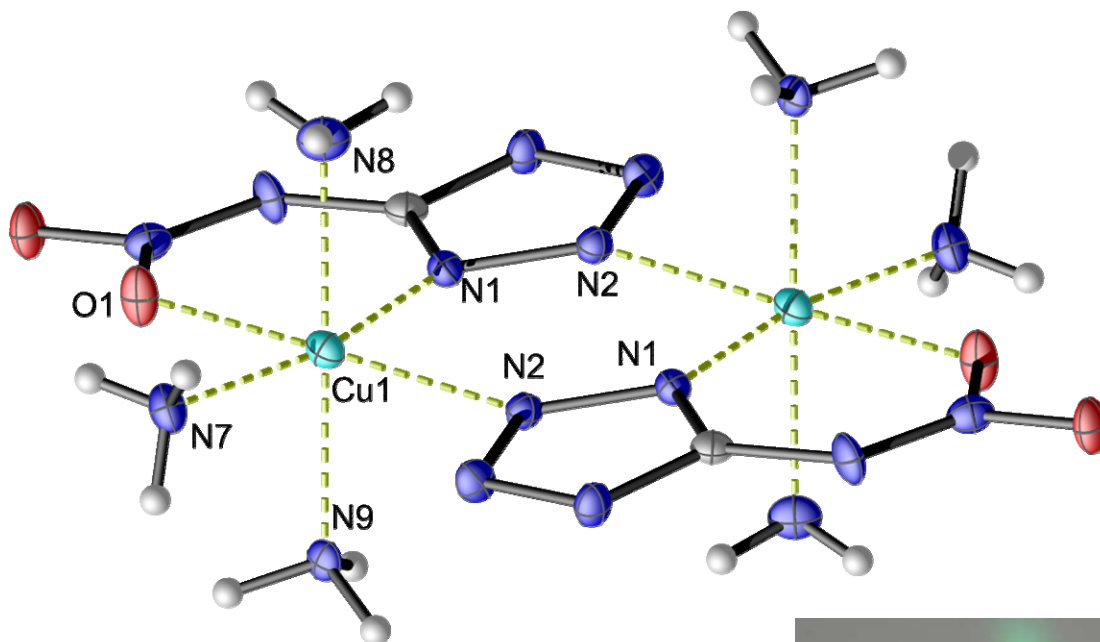
2.1 *trans*-Tetra-aqua-bis-5-nitriminotetrazolato-*N*(4) copper(II)



$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (323 mg, 2 mmol) and 5-nitriminotetrazole (524 mg, 4.0 mmol) were dissolved in 12 ml water and heated to 90 °C for 10 minutes. The green-blue solution was left for crystallization. After three days light blue crystals suitable for XRD were obtained. (503 mg, yield 64 %)

m.p.: 110 °C ($-\text{H}_2\text{O}$), 128 °C (Dec.) DSC (5 deg/min). **IR** (KBr) $\tilde{\nu}[\text{cm}^{-1}]$: 3431 (s), 3100 (m), 1650 (m), 1540 (m), 1494 (w), 1457 (s), 1370 (m), 1324 (s), 1259 (s), 1159 (m), 1099 (w), 1063 (m), 1008 (w), 881 (w), (803 (w), 774 (w), 744 (m), 694 (w), 569 (w), 486 (w). **EA** ($\text{C}_2\text{H}_{10}\text{CuN}_{12}\text{O}_8$, 393.72): calc.: C 6.10 %, H 2.56 %, Cu 16.14 %, N 42.69 %, O 32.51 %; found: C 6.22 %, H 2.65 %, N 42.52 %. **impact** sens.: <30 J; **friction** sens.: < 300 N.

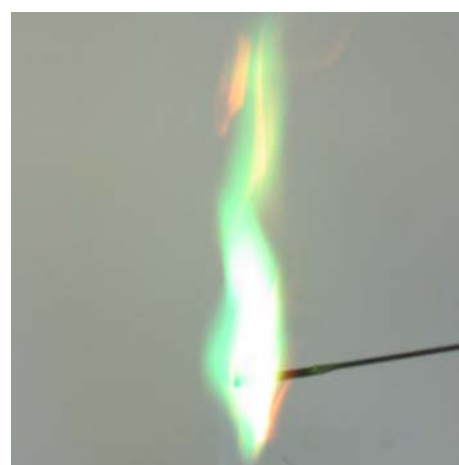
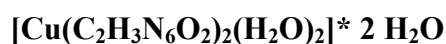
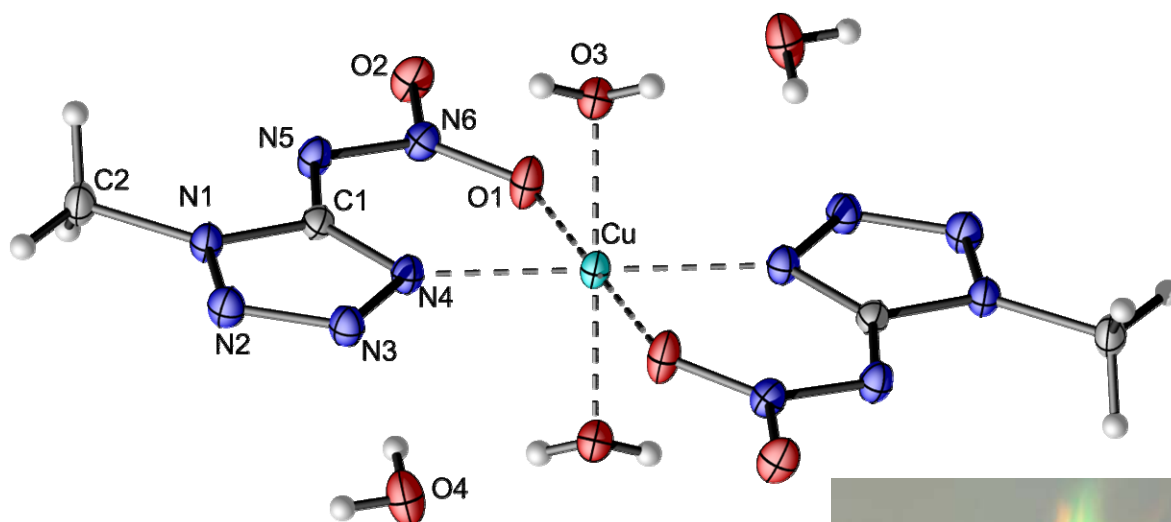
2.2 triamino-5-nitraminetetrazolato- *N,O* copper (II)



Copper(II)chlorid dihydrate (171 mg, 1.0 mmol) was dissolved in 2 mL of hot water and combined with a hot solution of 5-nitriminotetrazole (260 mg, 2 mmol) in 10 mL aqueous ammonia solution (25 %). After cooling to room temperature and waiting for 24 hours the product started to precipitate forming blue crystals. (203 mg, yield 42 %)

m.p.: 220 °C (dec.); **IR** (KBr, cm⁻¹): $\tilde{\nu}$ = 3332 (s), 3242 (s), 3168 (s), 2605 (w), 2477 (w), 2362 (w), 2346 (w), 2294 (w), 2175 (w), 2019 (w), 1934 (w), 1891 (w), 1762 (w), 1733 (w), 1627 (m), 1462 (s), 1462 (s), 1399 (s), 1371 (s), 1303 (s), 1251 (s), 1237 (s), 1214 (m), 1153 (m), 1135 (w), 1094 (m), 1026 (s), 866 (m), 753 (m), 738 (m), 721 (w), 699 (w), 636 (w), 482 (w); **EA** (CH₉CuN₉O₂, 242.69): calcd.: C, 4.95; H, 3.74; Cu, 26.18; N, 51.94; O, 13.19; found: C, 4.98; H, 3.42; N, 51.93 %. **impact** sensitivity: 50 J; **friction** sensitivity: > 360 N.

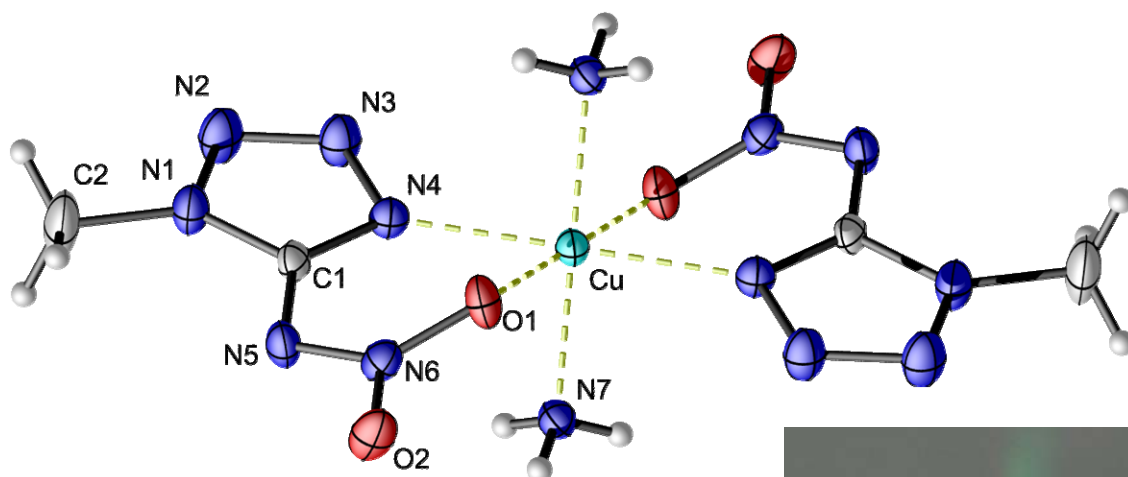
2.3 Bis(1-methylnitriminotetrazolate)copper(II) tetrahydrate



Copper(II)nitrate trihydrate (240 mg, 1.0 mmol) was dissolved in 2 mL hot water and combined with a hot solution of 1-methyl-5-nitriminotetrazole (288 mg, 2 mmol) in 15 ml water and refluxed for 5 min. After cooling to room temperature and waiting for 24 hours blue crystals of **14** started to precipitate. (299 mg, yield 71 %) After filtration the mother liquid was left, whereby green crystals of **15** were obtained. (39 mg, yield 10 %)

m.p.: 256° C (dec.); **IR** (KBr, cm^{-1}): $\tilde{\nu}$ = 3504 (m), 3461 (m), 3220 (m), 2963 (m), 2148 (w), 1801 (w), 1662 (w), 1526 (m), 1476 (s), 1398 (m), 1384 (m), 1339 (s), 1305 (s), 1256 (m), 1120 (m), 1037 (m), 1010 (w), 929 (w), 887 (w), 859 (w), 776 (w), 737 (w), 654 (w), 585 (w); **EA** ($\text{C}_4\text{H}_{14}\text{CuN}_{12}\text{O}_8$, 421.78) calcd.: C, 11.39; H, 3.35; Cu, 15.07; N, 39.85; O, 30.35 %; found: C, 11.32; H, 3.38; N, 39.69 %. **impact** sensitivity: > 50 J; **friction** sensitivity: > 360 N.

2.4 Diamino-bis(1-methylnitriminotetrazolate)copper(II)



Copper(II)nitrate trihydrate (483.2 mg, 2 mmol) was solved in 2 ml of hot ammonia (25 %). After solving 5-nitramino-1-methyl-tetrazole (576 mg, 4 mmol) in 10 mL of hot ammonia (25%), both solution were combined, refluxed for 5 min and left for crystallization. The purple cube-shaped crystals obtained were suitable for X-ray diffraction. (750 mg, 98 %)

m.p.: 243 °C (dec.); **IR** (KBr, cm^{-1}): $\tilde{\nu}$ = 3450 (w), 3330 (m), 3188 (m), 3042 (w), 1784 (w), 1632 (m), 1522 (w), 1473 (s), 1412 (s), 1379 (m), 1324 (s), 1287 (s), 1242 (s), 1123 (m), 1054 (w), 1030 (m), 877 (w), 757 (m), 703 (m), 689 (m), 496 (w); **EA** ($\text{C}_4\text{H}_{12}\text{CuN}_{14}\text{O}_4$, 383.78): calc.: C, 12.52; H, 3.15; Cu, 16.56; N, 51.10; found: C, 12.37; H, 3.19; N, 50.79 %. **impact** sensitivity: 12 J; **friction** sensitivity: < 280 N.

Part III: Structural and initial explosive properties of triaminotriazolium picrate and azotetrazolate

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3 Abstract

Two new highly stable energetic salts were synthesized in reasonable yield by using the high nitrogen heterocycle 3,4,5-triamino-1,2,4-triazole and resulting on its picrate and azotetrazolate salts. 3,4,5-triamino-1,2,4-triazolium picrate (**1**) and azotetrazolate (**2**) were characterized analytically using spectroscopic as well as X-ray diffraction studies. Some explosive properties of both compounds were also determined such as the sensitivity to impact and friction, the thermal stability, the enthalpy of combustion.

Keywords: Insensitive energetic materials, azotetrazolate, picrate, triaminotriazole, analytical and explosive properties.

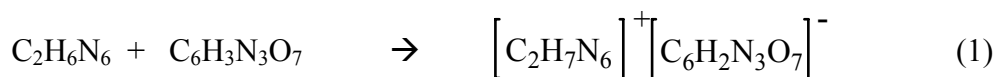
1 Introduction

Energetic salts based on high nitrogen heterocycles have been the subject of great interest in several research groups and particularly in ours [1, 2]. We much recently prepared and determined the analytical and explosive properties of 3,4,5-triamino-1,2,4-triazolium 5-nitrotetrazolate [3]. The triaminotriazolium classic salts (NO_3^- , ClO_4^- , $\text{N}(\text{NO}_2)^-$) have been recently reported [4, 5] as a new family of stable energetic materials. The neutral nitrogen-rich heterocycle (~74% nitrogen) can easily be synthesized from inexpensive and widely available starting materials [6, 7] and we have recently determined its complete characterization [3]. Here we report the synthesis with the analytical and explosive properties of two new energetic triaminotriazolium salts: the picrate salt (**1**) containing a high nitrogen heterocycle cation and an oxygen-rich anion forming a nitrogen-oxygen balance compound, and the azotetrazolate salt (**2**) based on two nitrogen-rich heterocycles.

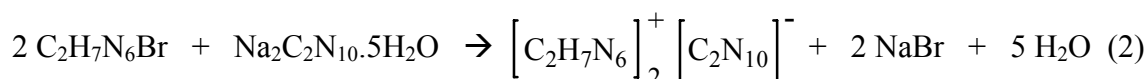
2 Results and Discussion

2.1 Synthesis

3,4,5-triamino-1,2,4-triazolium picrate (**1**) was prepared in good yield and purity from 3,4,5-triamino-1,2,4-triazole (guanazine) and picric acid (eq. 1, see experimental).



In order to obtain 3,4,5-triamino-1,2,4-triazolium azotetrazolate (**2**), 3,4,5-triamino-1,2,4-triazolium bromide (guanazinium bromide) and sodium azotetrazolate pentahydrate [8] were used as starting materials (eq. 2, see experimental).



2.2 Spectroscopy

Due to fast proton exchange in DMSO solution, no resonance supporting the ring protonation in the ^1H NMR spectrum was detectable. In the ^{13}C NMR spectrum, there was a slight shift in the triaminotriazolium carbons resonance as expected upon protonation but still in the expected region for sp^2 hybridized carbon of high nitrogen heterocycles [3]. In order to avoid quadrupolar broadening in the ^{14}N NMR spectrum, a ^{15}N NMR spectrum was recorded (natural abundance) in DMSO solution for compound (**1**) which showed six well resolved ^{15}N resonances at 3.2, -10.8 (-NO₂ groups of picrate), -177.1 (N-1,2), -238.9 (1N, N4), -323.4 and -330.2 ppm (-NH₂ groups of triaminotriazolium). A solid state $^{15}\text{N}\{^1\text{H}\}$ NMR experiment was carried out for compound (**2**) because of its very low solubility in the different solvents used in the liquid NMR technique. Thirteen ^{15}N resonances were observed for compound (**2**) in the area from +50 to -450 ppm, where the data was collected, and they were assigned as follows: 9.4, 4.7 and -0.9 ppm (CN _{α} two different sites crystallographically with disorder), -52.3, -63.0, -82.9 and -85.5 ppm (CN _{β} two different sites crystallographically with disorder), -188.9 and -189.2 ppm (N-1,2 crystallographically different), -239.9 ppm (1N, N4), -318.4, -323.9 and -330.0 ppm (3 NH₂ groups crystallographically different).

Both salts were analyzed by vibrational spectroscopy (see experimental), the IR spectra of (**1**) and (**2**) showed several strong bands in the N-H stretch region around 3400-3200 cm^{-1} . Strong evidence for the anion was observed in the Raman and IR spectra of both compounds: for (**1**) stretching vibrations of the picrate nitro groups were observed at 1370, 1316 and 1277 cm^{-1} in Raman and at 1329 and 1266 cm^{-1} in IR; for (**2**) stretching vibrations characteristic of the azotetrazolate anion were found at 1491 (ν_{azo}) and 1381 cm^{-1} ($\nu_{\text{C-Nazo}}$) in Raman and at 1391 (ν_{asN3C}) and 732 cm^{-1} (ν_{asN2C}) in IR.

2.3 X-ray structures

After recrystallization from water, crystals of 3,4,5-triamino-1,2,4-triazolium picrate (**1**) and azotetrazolate (**2**) suitable for single crystal X-ray structure determination were obtained. The molecular structures of (**1**) and (**2**) in the crystalline state are shown, as DIAMOND [9] projections, in figures 1 and 2. Both picrate and azotetrazolate salts crystallized in a triclinic cell with P-1 symmetry, details of the X-ray study are summarized in Table 1.

Table 1. Crystallographic data for (**1**) and (**2**).

| | 1 | 2 |
|--|--|--|
| Formula | C ₈ H ₉ N ₉ O ₇ | C ₆ H ₁₄ N ₂₂ |
| Formula weight [g mol ⁻¹] | 343.214 | 394.324 |
| Temperature (K) | 200 | 373 |
| Radiation used, wavelength | Mo-K α , 71.073 pm | Mo-K α , 71.073 pm |
| Crystal system | triclinic | triclinic |
| Space group | <i>P</i> -1 | <i>P</i> -1 |
| a [nm] | 0.37888(5) | 0.52619(9) |
| b [nm] | 1.28336(14) | 0.6698(2) |
| c [nm] | 1.39357(13) | 1.1884(8) |
| α [°] | 103.778(9) | 102.05(4) |
| β [°] | 90.383(9) | 90.80(3) |
| γ [°] | 96.943(10) | 109.96(2) |
| <i>V</i> _{UC} [nm ³] a | 0.65284(13) | 383.4(3) |
| Z a | 2 | 1 |
| ρ [g cm ⁻³] | 1.7460(3) | 1.708(1) |
| <i>F</i> (000) | 352 | 204 |
| θ range for data collection | 3.93° - 29.99° | 4.08° - 28.60° |
| Index ranges | -4 $\leq h \leq$ 4, -15 $\leq k \leq$ 15, -17 $\leq l \leq$ 17 | -6 $\leq h \leq$ 6, -8 $\leq k \leq$ 8, -13 $\leq l \leq$ 15 |
| Reflections collected | 6632 | 3845 |
| Independent reflections | 2560 (<i>R</i> _{int} = 0.0398) | 1680 (<i>R</i> _{int} = 0.0314) |
| Refinement method | Full-matrix least-squares on <i>F</i> ² | Full-matrix least-squares on <i>F</i> ² |
| Data/Restraints/Parameters | 2560 / 0 / 253 | 1680 / 0 / 164 |
| Goodness-of-fit on <i>F</i> ² | 1.083 | 0.908 |
| Weighting scheme | $w^{-1} = \sigma^2 F_0^2 + (0.1008 P)^2 + 0.0000$ <i>P</i> where $P = (F_0^2 + 2F_c^2)/3$ | $w^{-1} = \sigma^2 F_0^2 + (0.0438P)^2 + 0.0000P$ where $P = (F_0^2 + 2F_c^2)/3$ |
| <i>R</i> ₁ [<i>F</i> > 4 σ (<i>F</i>)] | 0.0542 | 0.0365 |
| <i>R</i> ₁ (all data) | 0.0671 | 0.0666 |
| <i>wR</i> ₂ [<i>F</i> > 4 σ (<i>F</i>)] | 0.1445 | 0.0764 |
| <i>wR</i> ₂ (all data) | 0.1581 | 0.0849 |
| Largest diff. peak and hole | 0.384 and -0.298 (10 ⁻³ nm ³) | 0.179 and -0.268 (10 ⁻³ nm ³) |

a *V*_{UC}: volume of unit cell; Z: number of molecules in unit cell.

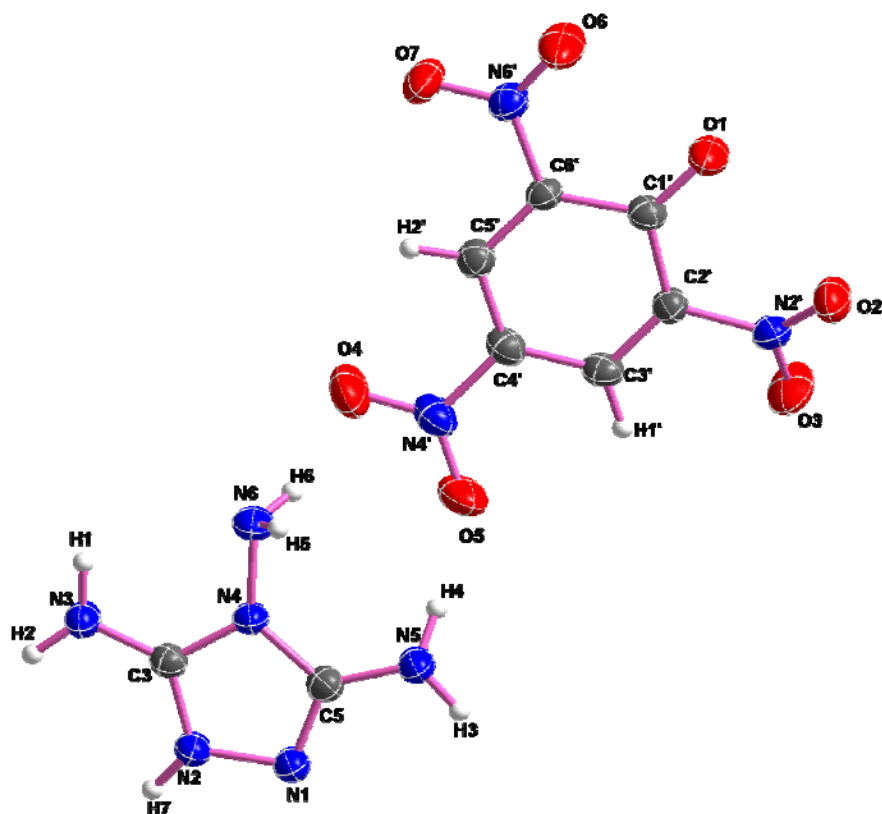


Figure 1. Molecular structure of **(1)** in the crystalline state. Displacement ellipsoids are shown at the 50% probability level.

2.4 Differential Scanning Calorimetry (DSC)

The DSC plots of 3,4,5-triamino-1,2,4-triazolium picrate **(1)** and azotetrazolate **(2)** are shown in figures 2 and 3 respectively. With a heating rate of $2^{\circ}\text{C min}^{-1}$, exothermic decomposition is detectable above 269°C with $\Delta H_{(1)} = -927.855 \text{ J g}^{-1}$ for **(1)** and above 212°C with $\Delta H_{(2)} = -1056.044 \text{ J g}^{-1}$ for **(2)**. No melting phase was detectable for both salts (decomposition, see experimental). DSC studies revealed a very high thermal stability for the picrate and azotetrazolate salts, which most likely can be attributed to the extensive hydrogen bonding observed in the crystalline state.

2.5 Bomb calorimetry

The experimentally determined values from three averaged measurements are:

$$\Delta H_{\text{comb.}}^{\text{exp.}}(\mathbf{1}) = 4179.8 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{comb.}}^{\text{exp.}}(\mathbf{2}) = 5412.4 \text{ kJ mol}^{-1}$$

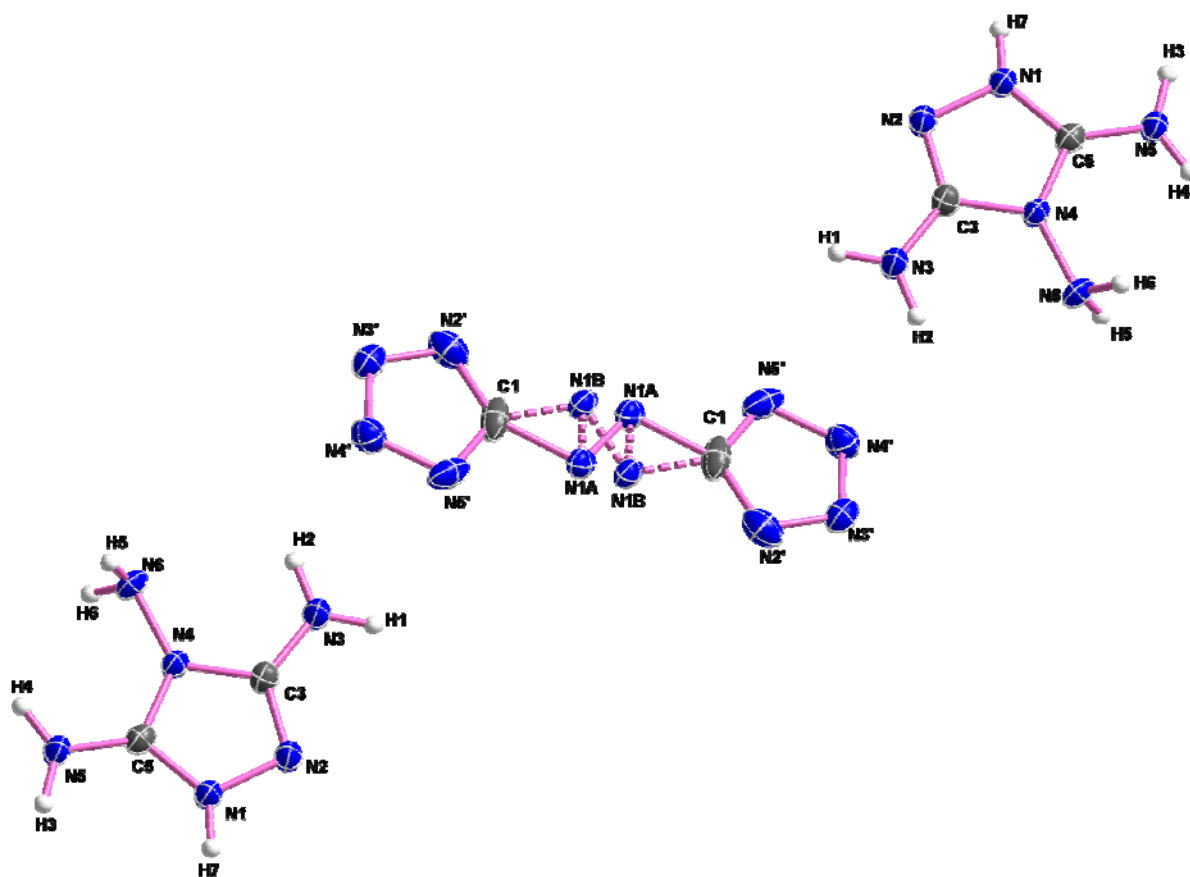


Figure 2. Molecular structure of **(2)** in the crystalline state showing a disorder in the azo group. Displacement ellipsoids are shown at the 50% probability level.

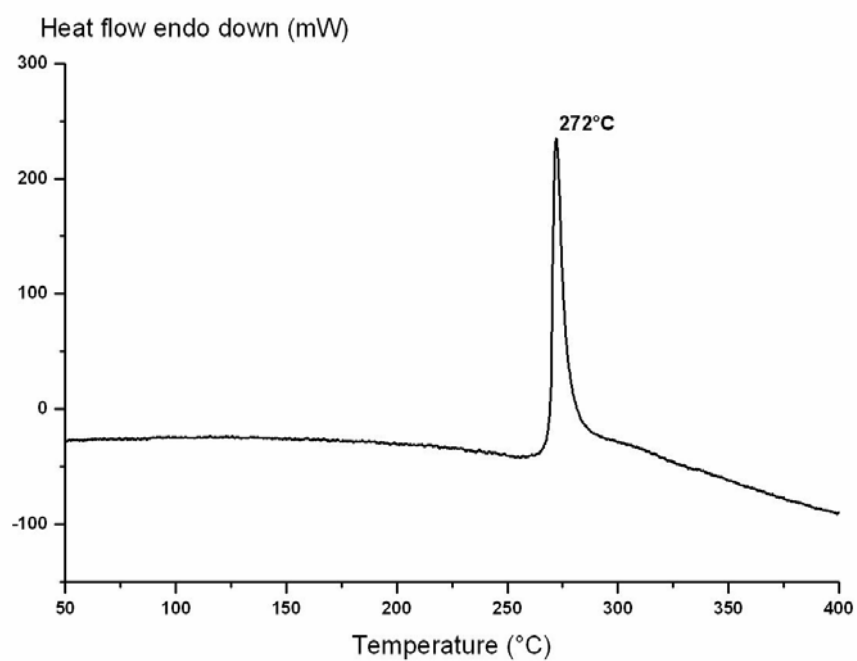


Figure 3 DSC plot of 3,4,5-triamino-1,2,4-triazolium picrate **(1)**, heating rate 2°C/min.

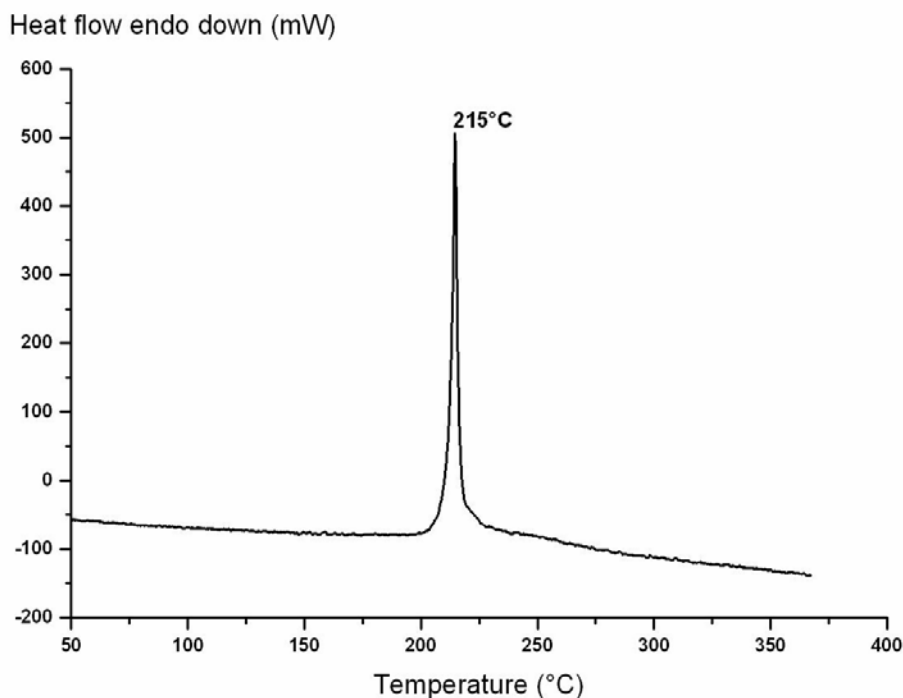


Figure 4 DSC plot of 3,4,5-triamino-1,2,4-triazolium azotetrazolate (**2**), heating rate 2°C/min.

2.6 Sensitivity Data

Both compounds showed no sensitivity to impact nor friction:

- Drophammer test [10, 11]: > 30 J (BAM method, 6 tests, 0 explosions @ 30 J)
- Friction test [11]: > 360 N (BAM method, 6 tests, 0 explosions @ 360 N)

4 Experimental

3.1 3,4,5-Triamino-1,2,4-triazolium picrate (**1**)

To an aqueous solution of 0.57 g (5 mmol) of 3,4,5-triamino-1,2,4-triazole (prepared as described in the literature [6]) was added 1.15 g of picric acid (1 wt.% in H₂O from Aldrich dried over 2 days at 60°C in the oven). This mixture was stirred and boiled for 30 minutes. The solvent volume was then reduced and allowed to cool yielding 1.48 g (~86%) of yellow crystals suitable for X-ray structure determination.

Raman $\Delta\nu$ /cm⁻¹ (rel. int.): 3301(5), 1568(30), 1559(34), 1370(69), 1340(69), 1316(100), 1300(88), 1277(40), 944(23), 826(71), 308(11).

Infrared (KBr Pellet); ν /cm⁻¹ (strong/medium/weak): 3401w, 3174m, 1706m, 1639m, 1541m, 1430w, 1329s, 1267s, 1156w, 908w, 786s, 712m.

Elemental Analysis: calcd. (C₈H₉N₉O₇), found / %: C 28.00, 28.10; N 36.73, 36.46; H 2.64, 2.85

M.P.: decomposition without melting at 270°C with black residue, Buechi B-540 melting point apparatus, uncorrected.

DSC decomposition onset: 269.4°C

^1H -NMR (DMSO- d_6 , 400.18 MHz, 25°C, TMS) δ /ppm: 8.56 (m, H_{arom}) 7.03 (broad s, 4H, - NH_2), 5.54 (broad s, 2H, - NH_2)

$^{13}\text{C}\{^1\text{H}\}$ -NMR (DMSO- d_6 , 100.63 MHz, 25°C, TMS) δ /ppm: 161.3 (C1'), 150.4 (C-3,5), 142.3 (C-2',4'), 125.7 (C-3',5'), 124.8 (C6')

$^{15}\text{N}\{^1\text{H}\}$ -NMR (DMSO- d_6 , 40.55 MHz, 25°C, MeNO_2) δ /ppm: 3.2 (1N, - NO_2), -10.8 (2N, - NO_2), -177.1 (2N, N-1,2), -238.9 (1N, N4), -323.4 (1N, NH_2), -330.2 (2N, NH_2).

3.2 3,4,5-Triamino-1,2,4-triazolium bromide

A mixture of 72 g (~ 1 mole) of dimethylcyanamide 97% (Acros organics) and 50 g (~ 1 mole) of hydrazine hydrate 98% (Aldrich) was refluxed for 24 hours [6]. The resulting solid mass obtained on cooling was treated with an excess of a concentrated solution of 48% hydrobromic acid in MeOH. A white solid precipitated, was filtered off and washed with a saturated solution of sodium carbonate in cold water. It was recrystallized from water yielding 68 g (70%) of 3,4,5-triamino-1,2,4-triazolium bromide.

Raman $\Delta\nu/\text{cm}^{-1}$ (rel. int.): 3238(7), 3162(7), 1699(11), 1671(19), 1451(12), 1381(10), 1315(12), 806(25), 774(100), 631(18), 343(13), 327(18), 181(11).

Infrared (KBr Pellet); ν/cm^{-1} (strong/medium/weak): 3306m, 3242w, 3114s, 1702s, 1659s, 1621s, 1527m, 1451m, 1381w, 1152w, 1017m, 920s, 799w, 769w, 692s.

Elemental Analysis: calcd. ($\text{C}_2\text{H}_7\text{N}_6\text{Br}$), found / %: C 12.32, 12.30; N 43.09, 43.12; H 3.62, 3.47

DSC melting onset: 269.6°C

^1H -NMR (DMSO- d_6 , 400.18 MHz, 25°C, TMS) δ /ppm: 7.20 (broad s, 4H, - NH_2), 5.91 (broad s, 2H, - NH_2)

$^{13}\text{C}\{^1\text{H}\}$ -NMR (DMSO- d_6 , 100.63 MHz, 25°C, TMS) δ /ppm: 150.4 (C-3,5)

$^{15}\text{N}\{^1\text{H}\}$ -NMR (DMSO- d_6 , 40.55 MHz, 25°C, MeNO_2) δ /ppm: -202.6 (2N, N-1,2), -239.0 (1N, N4), -320.2 (1N, NH_2), -328.4 (2N, NH_2).

3.3 3,4,5-Triamino-1,2,4-triazolium azotetrazolate (2)

To an aqueous solution of 1.24 g (4.13 mmol) of sodium azotetrazolate pentahydrate (prepared as described in the literature [8]) was added 1.6 g (8.22 mmol) of 3,4,5-triamino-1,2,4-triazolium bromide (prepared as described above). The mixture was stirred and boiled for 30 minutes and 3,4,5-triamino-1,2,4-triazolium azotetrazolate, slightly insoluble in hot water, formed a yellow suspension and precipitated when cooling. It was filtered out yielding 1.35 g (~83%) of yellow solid EA pure. A small amount was recrystallized from water to give yellow crystals suitable for X-ray structure determination.

Raman $\Delta\nu$ /cm⁻¹ (rel. int.): 3275(1), 1491(83), 1418(16), 1382(100), 1074(18), 1060(34), 1047(53), 1031(18), 923(15), 773(12), 360(3).

Infrared (KBr Pellet); ν /cm⁻¹ (strong/medium/weak): 3434w, 3178m, 1707m, 1658s, 1613m, 1443w, 1391m, 1102w, 1007w, 879s, 767m, 732s, 580s, 565s.

Elemental Analysis: calcd. (C₆H₁₄N₂₂), found / %: C 18.28, 18.12; N 78.15, 77.25; H 3.58, 3.70

DSC decomposition onset: 212.1°C

¹H-NMR (DMSO-d₆, 400.18 MHz, 25°C, TMS) δ /ppm: 6.49 (broad s, 4H, -NH₂), 5.52 (broad s, 2H, -NH₂)

¹³C{¹H}-NMR (DMSO-d₆, 100.63 MHz, 25°C, TMS) δ /ppm: 173.2 (C_{anion}), 150.3 (C-3,5)

¹⁵N{¹H}-RAMP CP MAS NMR (50.70 MHz, 27°C, TMS) δ /ppm: 9.4, 4.7 and -0.9 ppm (CN _{α} two different sites crystallographically with disorder), -52.3, -63.0, -82.9 and -85.5 ppm (CN _{β} two different sites crystallographically with disorder), -188.9 and -189.2 ppm (N-1,2 crystallographically different), -239.9 ppm (1N, N4), -318.4, -323.9 and -330.0 ppm (3 NH₂ groups crystallographically different).

4. Conclusions

From this combined experimental and theoretical study the following conclusions can be drawn:

- 3,4,5-triamino-1,2,4-triazolium picrate (**1**) and azotetrazolate (**2**) were synthesized in a good yield and purity
- The crystal structures of 3,4,5-triamino-1,2,4-triazolium picrate (**1**) and azotetrazolate (**2**) were determined by single crystal X-ray diffraction
- The picrate salt (**1**) containing a high nitrogen heterocycle cation and an oxygen-rich anion forming a nitrogen-oxygen balance compound, and the azotetrazolate salt (**2**) based on two nitrogen-rich heterocycles are both not impact (>30 J) nor friction (>360 N) sensitive and have a high thermal stability.

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PART IV: SYNTHESIS AND CHARACTERIZATION OF N-TRINITROETHYL DERIVATIVES OF NITROGEN CONTAINING COMPOUNDS

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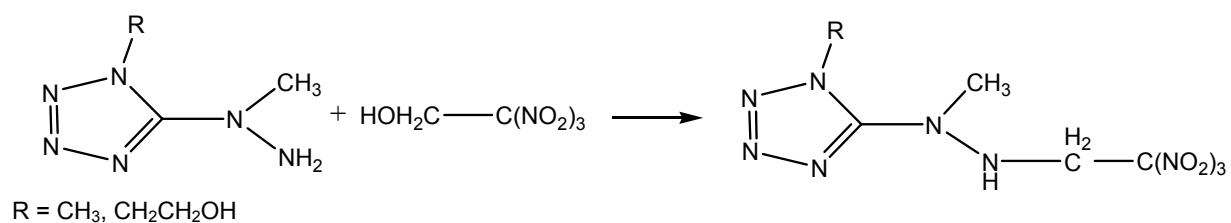
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1. INTRODUCTION

Although compounds carrying the N-trinitroethyl fragment have been reported, relevant data were published mainly in the patent literature, often without giving information about synthetic procedures or specifying the physicochemical characteristics of the compounds obtained. In the course of our investigations into high energy density materials, we recently focussed our attention to new derivatives of energetic materials that combine both the advantages of the tetrazole- as well as the trinitroethyl moiety. The tetrazole unit with its high nitrogen content together with its endothermic character is remarkably thermodynamically stable and the trinitroethyl fragment contributes to a positive oxygen balance.

2. SYNTHESIS

TNE and BTNA have been synthesized according to the literature [1, 2]. The synthetic approach for the synthesis of MTHT, MMTHT and MTHTE utilizes a condensation of the starting amino derivative with 2,2,2-trinitroethanol (Equation 1).



Equation 1.

3. STRUCTURAL ANALYSIS

Compounds **1-5** have been investigated using single crystal x-ray diffraction (Table 1, Figures 1-5).

TABLE 1. Selected structural parameters of 1-5.

| compound | TNE (1) | BTNA (2) | MTHT (3) | MMTHT (4) | MTHTE(5) |
|--|---|--|---|---|--|
| formula | C ₂ H ₃ N ₃ O ₇ | C ₄ H ₅ N ₇ O ₁₂ | C ₄ H ₇ N ₉ O ₆ | C ₅ H ₉ N ₉ O ₆ | C ₆ H ₁₁ N ₉ O ₇ |
| formula weight | 181.07 | 343.12 | 277.19 | 291.21 | 321.208 |
| temperature / K | 200 | 200 | 100 | 100 | 100 |
| crystal system | monoclinic | orthorhombic | orthorhombic | triclinic | monoclinic |
| space group | <i>P</i> 2 ₁ /c (no. 14) | <i>P</i> bca (no.61) | <i>P</i> bca (no.61) | <i>P</i> -1 (no.2) | <i>P</i> 2 ₁ /n (no.14) |
| a / Å | 6.1218(4) | 12.8996(6) | 9.7012(4) | 7.2651(13) | 13.0419(4) |
| b / Å | 18.8120(12) | 11.7753(5) | 12.8504(7) | 7.5773(16) | 7.3020(2) |
| c / Å | 11.7391(8) | 16.1577(7) | 17.3758(9) | 11.695(7) | 14.8002(5) |
| α / ° | 90 | 90 | 90 | 102.89(3) | 90 |
| β / ° | 104.997(4) | 90 | 90 | 103.82(3) | 112.118(4) |
| γ / ° | 90 | 90 | 90 | 99.387(17) | 90 |
| volume / Å³ | 1305.87(15) | 2454.30(19) | 2166.14(19) | 593.3(4) | 1305.73(7) |
| Z | 8 | 8 | 8 | 2 | 4 |
| absorption coefficient / mm⁻¹ | 0.191 | 0.188 | 0.156 | 0.146 | 0.147 |
| density exptl. / g / cm³ | 1.842 | 1.857 | 1.700 | 1.630 | 1.634 |
| F(000) | 736 | 1392 | 1136 | 300 | 664 |
| 2 theta / ° | 51.0 | 51.5 | 49.0 | 52.0 | 54.0 |
| reflections collected | 12556 [R _{int} = 0.0631] | 22836 [R _{int} = 0.0494] | 8573 [R _{int} = 0.1493] | 5201 [R _{int} = 0.0225] | 8966 [R _{int} = 0.0237] |
| reflections unique | 2424 | 2330 | 1784 | 2299 | 2813 |
| parameters | 237 | 228 | 172 | 217 | 243 |
| GOOF | 1.223 | 1.294 | 1.057 | 0.943 | 1.017 |
| R₁ / wR₂ [I > 2σ(I)] | 0.0651 / 0.1048 | 0.0802 / 0.1766 | 0.0836 / 0.1713 | 0.0293 / 0.0678 | 0.0286 / 0.0682 |
| R₁ / wR₂ (all data) | 0.0825 / 0.1135 | 0.0831 / 0.1787 | 0.1517 / 0.2106 | 0.0426 / 0.0716 | 0.0425 / 0.0732 |

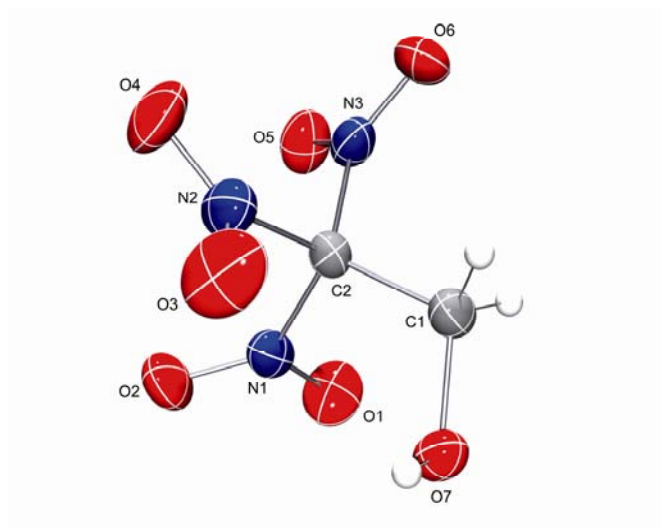


Figure 1. ORTEP representation of the molecular structure of TNE in the crystalline state. The thermal ellipsoids are shown at the 50 % probability level.

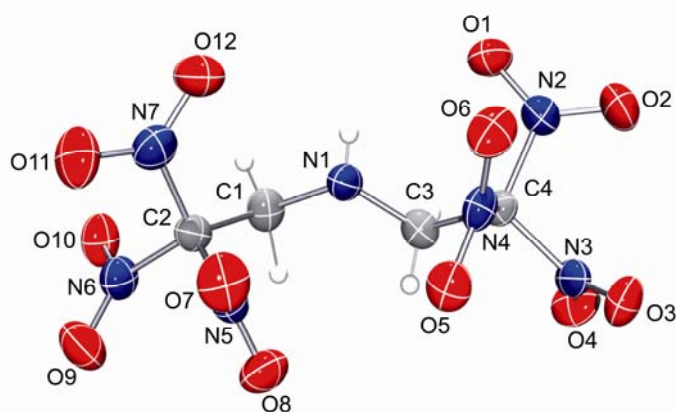


Figure 2. ORTEP representation of the molecular structure of BTNA in the crystalline state. The thermal ellipsoids are shown at the 50 % probability level.

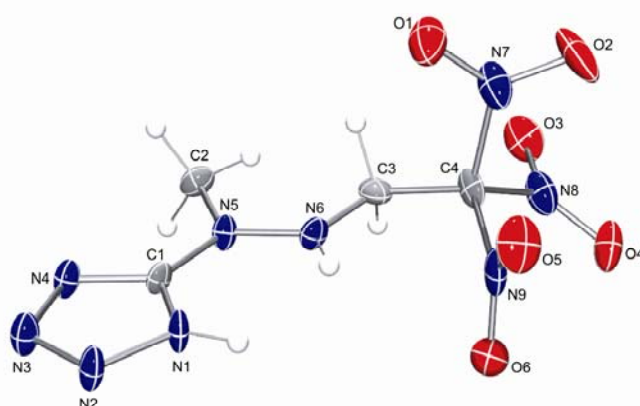


Figure 3. ORTEP representation of the molecular structure of MTHT in the crystalline state. The thermal ellipsoids are shown at the 50 % probability level.

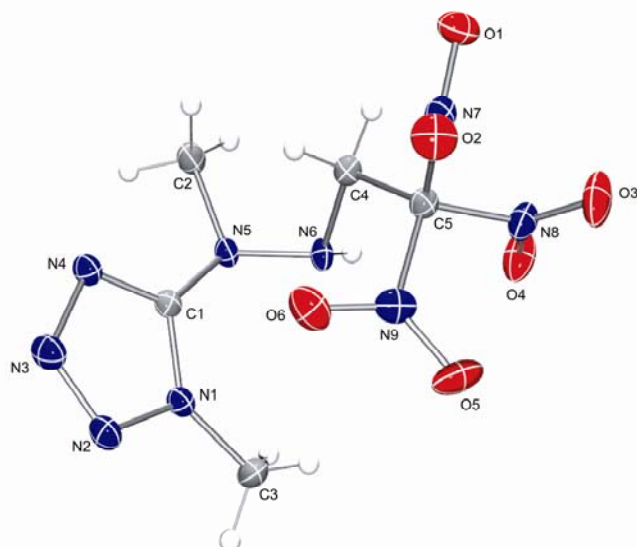


Figure 4. ORTEP representation of the molecular structure of MMTHT in the crystalline state. The thermal ellipsoids are shown at the 50 % probability level.

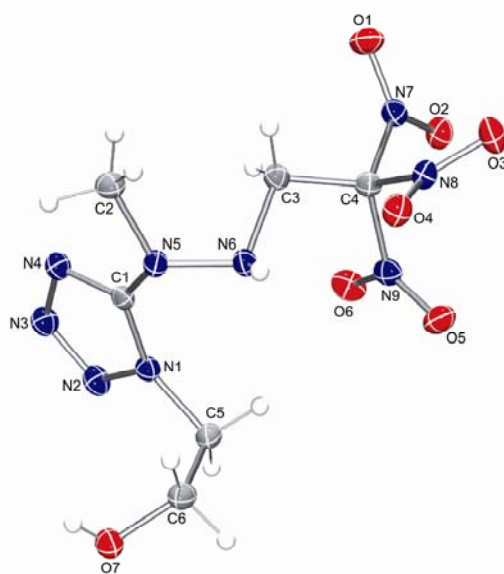


Figure 5. ORTEP representation of the molecular structure of MTHTE in the crystalline state. The thermal ellipsoids are shown at the 50 % probability level.

EXPERIMENTAL

Trinitroethanole, *TNE*

^1H NMR ([D6]acetone) δ : 5.17 (2H, d, $^3J=5.6$ Hz), 6.32 (1H, t, $3J=5.6$ Hz); ^{13}C NMR ([D6]acetone) δ : 63.1 (d, $-\text{CH}_2-$), 127.5 (bs, $-\text{C}(\text{NO}_2)_3$); ^{14}N NMR ([D6]acetone) δ (nitromethane): 30.8 ($-\text{NO}_2$); Raman (100 mW, 20 scans, protection shield, 2 cm^{-1}) $\tilde{\nu}/\text{cm}^{-1}$: 3012 w, 2965 w, 1606 w, 1444 w, 1397 w, 1375 w, 1352 s, 1312 w, 1101 w, 1004 w, 883 w, 858 vs, 809 w, 779 w, 536 w, 423 s, 405 s, 373 vs, 290 w, 222 w, 202 w, 173 w; IR (pure solid substance) $\tilde{\nu}/\text{cm}^{-1}$: 3410 (w), 3317 (w), 1691 (w), 1623 (m), 1583 (vs), 1488 (m), 1439 (m), 1408 (m), 1372 (m), 1350 (m), 1308 (vs), 1297 (vs), 1254 (s), 1244 (s), 1160 (w), 1088 (vs), 1060 (s), 1043 (m), 1024 (w), 1007 (w), 964 (w), 882 (m), 856 (m), 803 (vs), 780 (vs), 713 (m), 696 (w), 657 (m); $T_{\text{melt.}}$: 38.6°C (onset, $2^\circ\text{C}/\text{min}$, Linseis DSC), $T_{\text{decomp.}}$: 100.3°C (onset, $2^\circ\text{C}/\text{min}$, Linseis DSC); $\Delta U_{\text{comb.}}$ (exp.): $1.42(19)$ kcal/g.

Bis(trinitroethyl)amine, BTNA

Raman (300 mW, 120 scans, protection shield, 1 cm^{-1}) $\tilde{\nu}/\text{cm}^{-1}$: 3011 (8), 2982(13), 2949(24), 1607(27), 1445 (20), 1431 (11), 1398 (16), 1377 (15), 1354 (43), 1311 (41), 1260 (8), 859 (100), 809 (8), 782 (8), 663 (8), 644 (10), 562 (9), 536 (11), 423 (47), 397 (50), 376 (90), 299 (19), 280 (22), 213 (24); IR (pure solid substance) $\tilde{\nu}/\text{cm}^{-1}$: 3406 (w), 3370 (m), 2987 (w), 2946 (w), 2894 (w), 1582 (vs), 1478 (s), 1442 (s), 1431 (m), 1408 (w), 1397 (w), 1376 (m), 1350 (w), 1339 (w), 1307 (vs), 1298 (vs), 1258 (s), 1243 (m), 1156 (m), 1133 (m), 1089 (m), 1059 (w), 1049 (m), 1020 (w), 1008 (w), 883 (m), 873 (m), 854 (s), 803 (vs), 791 (vs), 781 (vs), 751 (w), 740 (m), 712 (w), 660 (m), 642 (s); $T_{\text{decomp.}}$: 82.6°C (onset, $2^\circ\text{C}/\text{min}$, Linseis DSC); MS (DEI, 70eV): 343 [m^+], MS (HR): calculated for BTNA: 342.9996 found: 342.9970 (-2.6 mmu).

5-(1-methyl-2-(2,2,2-trinitroethyl)hydrazinyl)-1H-tetrazole, *MTHT*

Raman (100 mW, 100 scans, protection shield, 1 cm⁻¹) $\tilde{\nu}$ /cm⁻¹: 3287 (39), 2996 (21), 2948 (43), 2826 (14), 1627 (34), 1605 (42), 1464 (24), 1450 (23), 1413 (38), 1403 (41), 1349 (48), 1303 (41), 1285 (36), 1228 (19), 1114 (25), 1086 (38), 1063 (25), 1038 (28), 998 (25), 971 (30), 856 (100), 800 (17), 779 (15), 740 (15), 656 (23), 629 (19), 541 (21), 449 (31), 404 (72), 372 (75), 312 (28), 255 (30), 202 (29), 187 (30);

IR (pure solid substance) $\tilde{\nu}$ /cm⁻¹: 3286 (w), 2992 (w), 2946 (w), 2890 (w), 2736 (w), 1774 (w), 1582 (vs), 1475 (w), 1410 (w), 1386 (w), 1348 (w), 1298 (s), 1225 (m), 1162 (w), 1126 (w), 1061 (m), 1035 (m), 992 (w), 964 (w), 876 (w), 854 (w), 834 (w), 796 (vs), 776 (s), 738 (m), 709 (w), 690 (w), 655 (w); T_{decomp.}(Büchi melting point apparatus, 5°/min): 100°C.

1-methyl-5-(1-methyl-2-(2,2,2-trinitroethyl)hydrazinyl)-1H-tetrazole, *MMTHT*

IR (pure solid substance) $\tilde{\nu}$ /cm⁻¹: 3342 (m), 2974 (w), 2941 (w), 2903 (w), 1610 (m), 1571 (vs), 1474 (s), 1458 (m), 1430 (m), 1419 (m), 1405 (w), 1391 (w), 1354 (w), 1308 (s), 1298 (s), 1265 (w), 1235 (w), 1202 (w), 1143 (m), 1122 (w), 1107 (w), 1045 (w), 879 (w), 858 (w), 821 (m), 797 (vs), 770 (s), 755 (m), 717 (w), 663 (w); T_{decomp.}: 82.5°C (onset, 2°C/min, Linseis DSC); C₅H₉N₉O₆: calc.: N (43,29%), C (20,62%), H (3,12%), found: N (43,09%), C (20,92%), H (3,29%); impact sensitivity: > 30J, friction sensitivity: 108N, $\Delta U_{\text{comb.}}$ (exp.) 2936 cal/g, Ω = -46.7%, Q_v: -6368 kJ/kg, T_{ex}: 4404 K, P_D: 277 kbar, V_D: 8307 m/s, V₀: 783 L/kg.

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